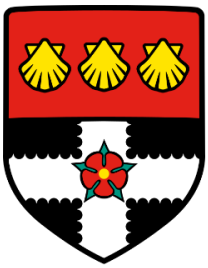

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Optimisation of oil recovery from sludges with surfactants and co-solvents

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Thesis submitted for the degree of Doctor of Philosophy

September 2016

Declaration

I confirm that this is my own work and the use of all material from other sources has been properly and fully acknowledged.

Signed:

Date:

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Firstly, I am greatly thankful to my supervisors Prof. Chris Collins and Dr. Liz Shaw for accepting me as their student and for all their scientific support, encouragement, and guidance throughout the PhD. Also, I would like to thank Dr. Radoslaw Kowalczyk for his help and support with the nuclear magnetic resonance data acquisition and analysis and Dr. Paula Jauregui and Prof. Vitaliy Khutoryanskiy for allowing me to characterise the surfactants in their labs. Also, I thank Dr. Shovonlal Roy and Mr. Alessandro Leidi for helping me organising the experimental design and the statistical analysis. I would like to extend my thanks to Karen, Anne, Alice, Mark, Alan, Geoff, Naomi, Richard, and Chris for all the valuable technical support in the lab. I am thankful to my colleagues in the research group, Koki, Amudat, Sarah, Ben, Mark, for all their advice and help throughout these years, and especially to Sonia, Katerina, and Jelena, for the guidance in the lab and for being very kind and supportive.

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Abstract

Oil sludges are composed mainly of crude oil, water and sediments. These are hazardous wastes from petroleum extraction and refining processes, and the worldwide generation of oil sludges is approximately 60 million tonnes per year. Treatment of oil sludges to date has been focused on physicochemical and biological remediation. Oil recovery methods including oil sludge washing with surfactants and co-solvents have also been applied for re-using the oil. However, there is a need to optimise the oil recovery in this process. The main aim of this research was to assess whether the addition of surfactants (Triton X-100 and X-114, Tween 80, sodium dodecyl sulphate, and rhamnolipid) and the co-solvents (*n*-pentane, *n*-hexane, cyclohexane, toluene and iso-octane) in the oil sludge washing enhances the oil recovery and reduces the burden of hydrocarbon contamination. Specifically, three oil sludge washing parameters were considered: surfactant to oil sludge ratio, surfactant type and surfactant concentration. Also, the influence of the co-solvent type and ratio to oil sludge was investigated. Oil sludges from different sources were analysed, and the toxicity of the residuals from oil sludge washing was assessed with the impact on the soil microbial respiration (dehydrogenase activity test) and ryegrass germination.

Rhamnolipid, Triton X-100 and Triton X-114 had the highest oil recovery rates (50 – 70%) compared to SDS and T80. These values were higher compared to other studies (30 – 40%). It was demonstrated that the ratio of surfactant to oil sludge factor had a high impact on the oil sludge washing. Particularly, it was found that the surfactant concentration did not have an effect on the oil recovery, and the addition of surfactant was not significantly different in most of the oil sludges analysed. Only one sludge had a highly significant oil recovery rate when surfactants were used. Cyclohexane, as a more benign co-solvent, was confirmed to have similar oil recovery values to toluene; approximately 75% of recovered oil was obtained with each co-solvent. This work has confirmed that oil sludge washing was an efficient pretreatment method which can reduce the organic contaminant. According to the oil hydrocarbon fractions analysed, the recovered oil had the potential to be reused as a feedstock for light fuel production. The oil sludge washing residuals had an adverse impact on the soil microbiota activity (percentage decrease of 40%), and ryegrass germination. However, some dehydrogenase activity by the soil bacteria and a germination higher than 70% were detected implying that bioremediation techniques can be applied to treat the oil sludge washing residuals further if necessary.

Based on these studies, a systematic approach to the extraction of oil from sludges was proposed at both laboratory and large scales. First, a quick bench scale experiment can be done to assess the oil recovery rates with surfactant and without surfactant at a low and high surfactant to oil sludge ratios (e.g. 1:1 and 5:1). By doing this first assay, it can be established if the surfactant is needed or not. If the surfactant is not required, the costs can be reduced. For this first assay, the surfactant can be added at lower concentrations because the results of this thesis showed no significant difference in the surfactant concentrations. The proposed application of this method to a large scale mentioned the possibility of adapting surfactant and co-solvent recycling systems to reuse these reagents in more cycles of oil sludge washing. The residual water obtained from the surfactant recycling step and the sediments at the bottom layer of the oil sludge washing tank can be mixed and considered as oil sludge washing residuals. Finally, these residuals can be further treated if needed with the landfarming and phytoremediation combined method in a designated area. Moreover, the use of soybeans was proposed as the phytoremediator species because these plants can also be used for biodiesel production purposes. Even though the oil sludge washing is a low-cost process compared to other treatments, the cost of applying the surfactant and solvent recycling systems is high due to the expensive equipment. In fact, it was found that about 70% of the total cost of the proposed method at a large scale goes towards these recycling systems. Indeed, it is important to consider the surfactant and co-solvent recovery steps carefully. However, if the proposed method is used on a frequent basis, the investment may be recuperated due to the profit obtained with the use of recovered oil as a feedstock for fuel production. In addition, if the phytoremediation with soybeans of the oil sludge washing residuals is implemented, the production of biodiesel can be a profitable source.

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Glossary of Acronyms

ACS	American Chemical Society
AEs	Alcohol ethoxylates
Agg.	Micellar Aggregation Number
ANP	Brazilian National Agency of Petroleum, Natural Gas and Biofuels
ANH	National Hydrocarbons Agency (from Colombia)
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BBO	Broadband Observe
BTEX	Benzene, toluene, ethylbenzene, and xylene
CAPB	Cocamidopropyl betaine
CCME	Canadian Council of Ministers of the Environment
CEN	European Committee for Standardisation
CFU	Colony-forming units
CEU	Council of the European Union
CMC	Critical micelle concentration
C/N	Carbon/nitrogen ratio
cP	centipoise (unit of viscosity)
CPMG	Carr-Purcell-Meiboom-Gill
CTAB	Hexadecyl(cetyl)trimethyl ammonium bromide
C/OS	Co-solvent to oil sludge ratio

DAF	Dissolved air flotation
DHA	Dehydrogenase activity test
DLS	Dynamic light scattering
dpi	Dots per inch
EA	Emulsifying agents
EC	European Community
EHS	Environmental, Health and Safety
EOR	Enhanced oil recovery
EO	Ethylene oxide
EPHs	Extractable petroleum hydrocarbons
fps	Frames per second
FRTR	Federal Remediation Technologies Roundtable
GC-FID	Gas chromatography with a flame ionisation detector
GLM	General linear model
GDP	Gross domestic product
HLB	Hydrophile-lipophile balance
HPLC	High performance liquid chromatography
HSP	Hansen solubility parameter
ICP-OES	Inductively coupled plasma optical emission spectrometry
INT	Iodonitrotetrazolium chloride
INTF	Iodonitrotetrazolium formazan
IPIECA	International Petroleum Industry and Environmental Conservation Association
JETRO	Japan External Trade Organization

kbpd	Thousand barrels per day
K_{ow}	Octanol-water partition coefficient
LPG	Liquefied petroleum gas
MADEP	Massachusetts Department of Environmental Protection
MAFF	Ministry of Agriculture, Fisheries and Food
MEOR	Microbial enhanced oil recovery
MEK	Methyl ethyl ketone
MEUF	Micellar-enhanced ultrafiltration
MW	Molecular weight
NAPLs	Non-aqueous phase liquids
NIBS	Non-invasive back scattering
NMR	Nuclear magnetic resonance
NSC	Oil refinery sludge (sample for this thesis)
NSO	Nitrogen, sulfur, and oxygen compounds
NTP	National Toxicology Program
ODS	Oil drilling sludge (sample for this thesis)
ORR	Oil recovery rate
OSW	Oil sludge washing
O/W	Oil-in-water
pA	Picoamps
PAHs	Polycyclic aromatic hydrocarbons
PBS	Phosphate buffer saline
PDI	Polydispersity index

PHCs	Petroleum hydrocarbons
POE	Polyoxyethylene
PTEs	Potentially toxic elements
Q	Research question
RCF	Relative centrifugal force
RF	Radiofrequency
RL	Rhamnolipid
RS	Waste engine oil sludge in centrifugation (sample for this thesis)
RSC	Royal Society of Chemistry
SBR	Sequencing batch reactor
SDBS	Sodium dodecyl benzene sulphonic acid
SDS	Sodium dodecyl sulphate
SETAC	Society of Environmental Toxicology and Chemistry
SEM	Standard error of the mean
SLS	Static light scattering
S/N	Signal-to-noise ratio
S/OS	Surfactant to oil sludge ratio
SPE	Solid-Phase Extraction
ST	Surface tension
STS	Waste engine oil sludge in gravitational settling (sample for this thesis)
T_1	NMR longitudinal relaxations
T_2	NMR transverse relaxations
T80	Tween 80

TEO	Total extractable organics
TNRCC	Texas Natural Resource Conservation Commission
TOC	Total organic carbon
TPF	Triphenylformazan
TPHs	Total petroleum hydrocarbons
TTC	Triphenyltetrazolium chloride
TX100	Triton X-100
TX114	Triton X-114
UCM	Unresolved complex mixture
USEPA	United States Environmental Protection Agency
VPHs	Volatile petroleum hydrocarbons
W/O	Water-in-oil emulsion
WSS	Water separator sludge (sample for this thesis)

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Chapter 1 - Introduction

1.1. Introduction

According to the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (2010), the world production of petroleum is around 12,600,000 $m^3 \cdot day^{-1}$, and 190,000 m^3 of oil sludge are generated each day. The oil production, transportation, and storage activities can produce these sludges (Wang *et al.*, 2010; Zhang *et al.*, 2011b). Figure 1.1A shows a general schematic diagram of the sources or inputs of oil sludges. Oil sludges (Figure 1.1B) are wastes containing a complex mixture of oil hydrocarbons, water, mineral solids, metals, and other chemicals generated in the petroleum refining process (Hu *et al.*, 2013).

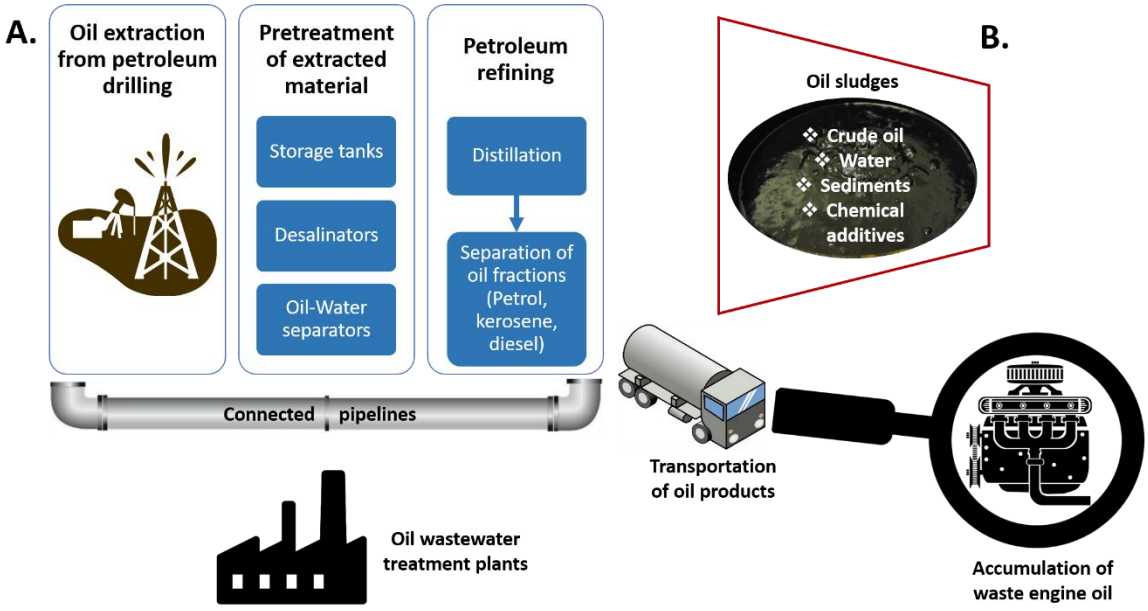

Figure 1.1. (A) Schematic diagram of the sources of oil sludge. (B) The main composition of oil sludges. All images are free licensed by Creative Commons.

The oil sludges can be generated at the first stage of crude oil extraction and pretreatment of crude oil (removal of water and sediments from the drilling). In fact, these wastes are found in crude oil storage tanks, desalinators, and oil-water separators. When the crude oil is refined

and separated into oil products, some unseparated emulsions can remain and cause sludge formation at the bottom of the storage tanks. Also, oil sludges can be formed after washing the pipelines in the oilfield and the tanker trucks that transport the oil related products. Particularly, the accumulation of waste oil and lubricant in motor engines can cause the formation of oil sludges. In addition, the tanks found in the oil wastewater treatment plants can have some formation of oil sludges at the bottom (Figure 1.1). According to Rahman et al. (2003) and Hu et al. (2013), the main sources of oil sludge production are crude oil storage tanks and oil-water separation systems. However, the oil tank bottom sludges are the most studied sludges (Rahman *et al.*, 2003; Hu *et al.*, 2013). Due to the wide range of sources of oil sludge, there is a need to find alternatives to treat these wastes efficiently. Figure 1.2 shows an overview of the current methods for treatment of the oil sludges.

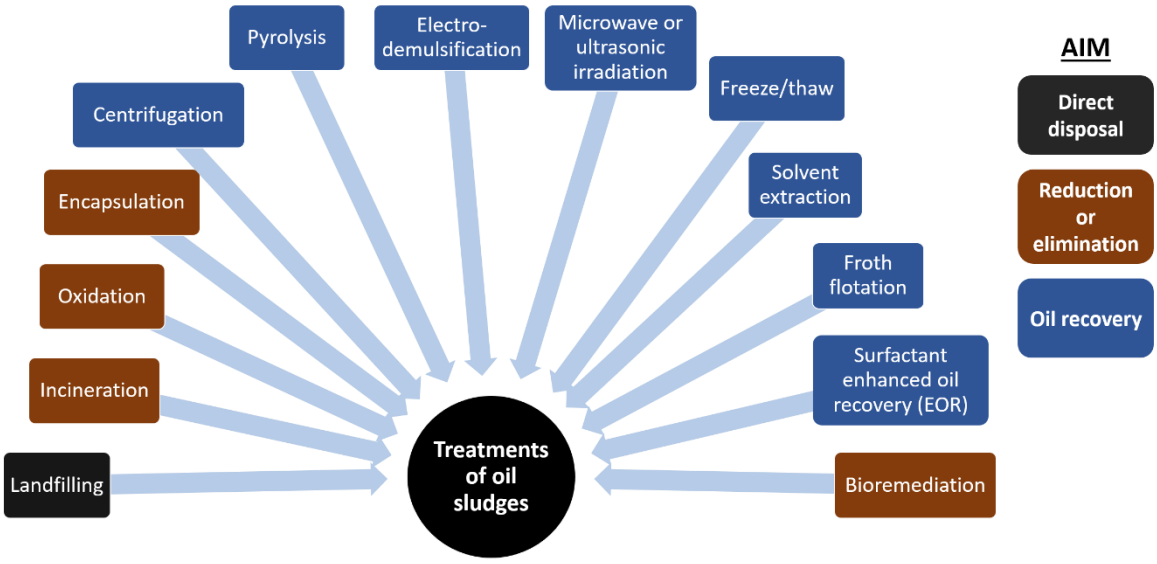

Figure 1.2. Overview of the current treatments of oil sludges. The treatments are grouped regarding the intended aim of the method (top-right corner).

Landfilling is the only direct disposal method in which the sludge is disposed of in an allocated area without any further treatment. Sometimes this area is isolated with an impermeable layer to avoid leachates to the groundwater. If the intention is to reduce or eliminate the volume of oil sludge, then the options can be incineration, oxidation, and encapsulation. Specifically, the encapsulation method consists of solidification and stabilisation of the contaminants in the sludge. Then, the contaminants are converted into less

soluble and toxic forms. Another method that aims at reducing the volume of oil sludge is bioremediation. In this case, the use of organisms can degrade the petroleum hydrocarbons and accumulate or transform the heavy metals to less toxic forms. The bioremediation of oil sludges includes: landfarming in a selected soil area; biopiles and bioreactors with microorganisms; and phytoremediation by plants. Finally, the oil recovery strategies include a variety of methods that use physicochemical separation of the oil sludge to obtain the oil, water and sediments in different layers. Then, the recovered oil can be reused as a feedstock for fuel production. These techniques are centrifugation, freeze/thaw treatment, solvent extraction, froth flotation, and surfactant enhanced oil recovery (EOR). Other techniques use energy to recover the oil including pyrolysis, electro-demulsification, microwave irradiation, and ultrasonic irradiation. Particularly, pyrolysis is a reduction technique similar to the incineration treatment because the oil sludge is converted into light organic compounds and CO_2. Alternatively, pyrolysis can be an oil recovery method because there is a possibility to transform these light organic compounds into a liquid state which can be used as feedstock for fuel production. Due to the wide range of techniques, Chapter 2 (Section 2.6) presents a detailed critical review of the generalities, advantages and disadvantages of each treatment.

According to the **3R** International Scientific Conference, the management of wastes has to be focused on **R**eduction, **R**euse and **R**ecycling (Sakai *et al.*, 2011). Therefore, the treatments have been aimed at the recovery of oil from the sludge. In fact, oil sludge is considered as a valuable source of energy which can be reused as fuel (Shie *et al.*, 2000). Recently, oil sludge washing using surfactants has been reported as a feasible method to recover the oil (Zhang *et al.*, 2012).

Oil sludge washing (OSW) is a process derived from soil washing procedures, which use liquid solutions to remove contaminants from soil (Pacwa-Płociniczak *et al.*, 2011). Surfactants are used in the washing to reduce the interfacial tension of the water-in-oil (W/O) macroemulsion in the sludge, and the consequent agitation performed in the washing process leads to the breakdown of this emulsion (Rosen and Kunjappu, 2012). Co-solvents can be added with surfactants to aid in the extraction of oil (Schramm, 2000b). Also, the combination of surfactants and co-solvent modifies the properties of the interfacial film leading to the coalescence and separation of the emulsion (Sjöblom *et al.*, 1990). Due to the importance of surfactants in the OSW, there is a need for testing specifically different types of surfactants and the influence of their concentration and surfactant to oil sludge (S/OS) ratio in the oil recovery. These parameters have all been studied in oil drill cuttings washing studies (Yan *et al.*, 2011)

and multiple soil washing studies (Deshpande *et al.*, 1999; Urum *et al.*, 2003; Urum and Pekdemir, 2004; Urum *et al.*, 2006; Pornsunthorntawee *et al.*, 2008; Peng *et al.*, 2011; Zhang *et al.*, 2011a). However, very little is known about the interaction of surfactant type, surfactant concentration and S/OS ratio in the oil recovery from oil sludges obtained from different sources. As it mentioned above, most studies have focused on oil tank bottom sludges. Also, it is necessary to analyse the residuals from the oil sludge washing to determine if it is necessary to perform further treatments. Ecotoxicological tests are an alternative because these tests are sensitive to the bioavailable fraction of the contaminant. In addition, the ecotoxicological assessments can complement chemical analyses such as the determination of the total extractable petroleum hydrocarbons (EPH) concentrations (Wilke *et al.*, 2008). If there is a significant amount of contaminants in the residuals, further remediation treatments can be applied such as landfarming (i.e. bioremediation using microorganisms) and phytoremediation. In these treatments, the residual sludge from OSW washing can be added to a determined soil area. In addition, the phytoremediator plants can have further uses. Even though these plants are not suitable for food consumption due to potential accumulation of contaminants, other types of plant species can be used for energy production. For instance, soybeans can be used as phytoremediators and for the production of biodiesel (Liu *et al.*, 2010). Indeed, the latter use can be a profitable option.

1.2. Research motivation

The Colombian government funded this PhD project through its Administrative Department of Science, Technology, and Innovation (Colciencias). The sponsorship call (529-2011) send students abroad to do a PhD about areas and topics relevant to the current needs of Colombia, to then return and apply the knowledge in the country.

The exploration of oil in Colombia has been carried out for more than 20 years, and this activity has increased in the last decade (Tasciotti *et al.*, 2015). According to Colombia's National Hydrocarbons Agency (ANH for its Spanish acronym), the crude oil production in Colombia was 525 thousand barrels per day (kbpd) on 2005, and 944 kbpd on 2012 (ANH, 2013). This increase has contributed to the gross domestic product (GDP) by 5% (Gallego *et al.*, 2015). However, the oil industry in Colombia has been affected by accidental oil spills and also by attacks from the guerrillas over the last two decades of armed conflict in Colombia

(Jernelöv, 2010). Another problem is the generation of oil sludges as a consequence of the increasing oil extraction and production as mentioned before.

In fact, I worked on the treatment of oil sludges in my Master's thesis, specifically on the phytoremediation of a residual oil sludge that was treated with landfarming. The sludge was amended to the soil, and it had an initial TPH concentration of 27,650 $mg \cdot kg^{-1}$. It was found that the landfarmed oil sludge provided adequate soil conditions to grow jack beans (*Canavalia ensiformis*) that in turn rhizo- and phytoremediated residual aliphatic and aromatic hydrocarbons in the soil. There were no differences in the plant height and leaf area compared to the control and no evidence of phytotoxicity. In this study, the reduction of total petroleum hydrocarbons was 57% during four months of growing jack beans (Ramirez and Dussan, 2014).

The main finding of this study was that phytoremediation could be an option for treating these landfarmed sludges. However, the hydrocarbon contaminant burden has to be reduced in order to ensure the survival of the bioremedial species. Landfarming with microorganisms is a promising technique which is not expensive and it could be used to treat large amounts of sludge (See Chapter 2. Section 2.6.2). In this method, the oil sludge is spread over the fresh soil where the native or hydrocarbon-degraders consortia of microorganisms reduce the total petroleum hydrocarbons (TPH) levels (da Silva *et al.*, 2012). However, this treatment requires between 6 months to 2 or more years to decontaminate the sludge, as well as large land areas (Hu *et al.*, 2013). Also, sometimes the contaminant burden is much higher than the tolerable levels for microorganisms, so the landfarming cannot be applied. According to the United States Environmental Protection Agency (USEPA), TPH levels higher than 50,000 ppm, and potentially toxic elements (PTEs) or heavy metals concentrations higher than 2,500 ppm are toxic for most of the microbiota (USEPA, 2004). Therefore, this PhD evaluates oil recovery as a pretreatment of oil sludges. It was found that the oil recovery using oil sludge washing is a potential option to treat these sludges after reviewing the literature (Chapter 2). Moreover, this chapter presents a critical review of each method considering the advantages and disadvantages, and their current use in a laboratory or industrial scale.

The aim of this research is to add to current understandings of oil recovery from oil sludges using surfactants, by investigating the effect of different surfactants, co-solvents, surfactant mixtures (co-surfactants), and OSW parameters (surfactant type and concentration, and S/OS ratio) in the maximisation of oil recovery. By doing this, the oil can be reused depending on its quality, and the organic contaminant burden in the residual sludge can be reduced. In addition,

toxicity and chemical tests were done to evaluate the residual sludge from the OSW, so it can be decided whether these residuals need further treatment. Finally, very little is known about the treatment of oil sludges from other sources, such as oil/water separator and oil drilling sludges. Therefore, this research tested different types of oil sludges. The oil sludges analysed in this thesis were obtained from the oil drilling and refining processes, oil-water separators, and motor engines.

1.3. Research questions

The main question of this investigation is whether the addition of surfactants and co-solvents in the oil sludge washing process enhances the recovery of oil and reduces the burden of hydrocarbon contamination. It has to be clarified that this thesis was mainly focused on the organic contamination rather than the inorganic components of the sludge. Five sub-questions (Q) were formulated to answer the principal question:

Q1) How do the surfactant type, surfactant concentration, and S/OS ratio factors affect oil recovery from different sludges in the OSW process?

Q2) Do the physicochemical characteristics of surfactants and the mixture of two surfactants influence the efficiency of oil recovery in the OSW?

Q3) Are there any differences in the oil recovery of the co-solvents applied in the OSW with surfactants?

Q4) Are the residuals from the OSW (residual sludge with surfactant solution and sediments from sludge) toxic to the soil microbiota and ryegrass?

Q5) What are the practical and economic feasibilities of OSW?

1.4. Thesis structure

This thesis begins with a review of the current literature about the common physicochemical characteristics of oil sludges, including its sources and available treatments (*Chapter 2*). *Chapter 3* presents a description of the oil sludges and surfactants used, and *Chapter 4* shows the preliminary OSW study with an oil-water separator sludge. *Chapter 5* describes the co-solvent and surfactant mixture effects on the oil recovery in the same oil-water separator sludge. Then, the results from the OSW experiment in different sludges and the analysis of the OSW residuals are presented in *Chapter 6*. Finally, an overall conclusion (*Chapter 7*) recalls all the findings obtained in this PhD thesis and provides recommendations for the future. Also, this chapter discusses the practical and economic feasibilities of the oil sludge washing process. Figure 1.3 shows a vertical chevron list of the organisation of this thesis and a brief explanation of each chapter.

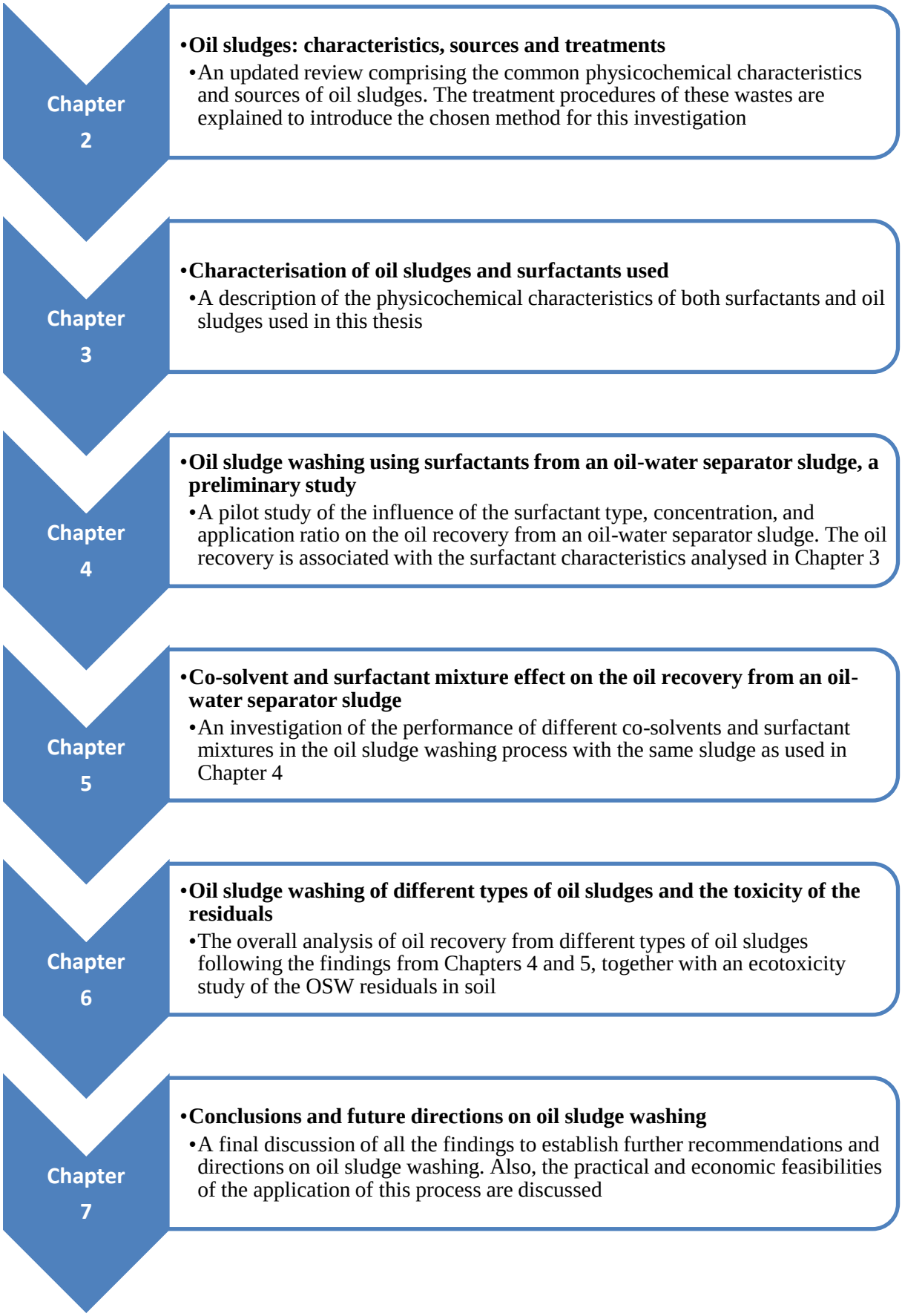

Figure 1.3. Structure of the thesis outlining the different chapters.

Initially, **Q1** is answered in *Chapter 4* with the preliminary study of the first oil sludge which was obtained from an oil-water separator. In addition, *Chapter 6* tests the effect of these factors (surfactant type and concentration, and S/OS ratio) on the oil recovery from different types of oil sludges. *Chapters 3 and 4* look at **Q2** by comparing the oil recovery of different surfactants with their characteristics such as micelle size, critical micelle concentration (CMC), and surface activity. The effect in the oil recovery of various co-solvents types and ratios to oil sludge (C/OS) (**Q3**) and surfactant mixtures (**Q2**) are analysed in *Chapter 5*. The same oil-water separator sludge from *Chapter 4* is used to answer these two questions. The second part of *Chapter 6* looks at **Q4** through the evaluation of ecotoxicity of the OSW residuals in soil by analysing the soil microbial activity with the dehydrogenase activity (DHA) test and the germination of ryegrass. The practical and economic feasibility of the application of OSW (**Q5)** is discussed in *Chapter 7*. Finally, all of these findings with their contributions to current knowledge and future directions on oil sludge washing are covered in this chapter.

1.5. Research outputs

The outputs of this thesis were presented at the following conferences:

- D. Ramirez and C. Collins (2014). Use of surfactants in the oil sludge washing process. Session: Organic Chemistry and Toxicity of Contaminants in the Ground. *Royal Society of Chemistry (RSC) Meeting*. London, UK.

- D. Ramirez and C. Collins (2015). Maximisation of oil recovery from an oil sludge washing process with surfactants. Session: Soil and water pollutants' assessment, monitoring and remediation. *Society of Environmental Toxicology and Chemistry (SETAC) Europe Annual Meeting*. Barcelona, Spain. **TU409**.

- D. Ramirez and C. Collins (2016). Oil recovery from oil sludges obtained from different sources using surfactants. Session: Oil and Gas Extraction: Ecological Effects and Science-Based Management. *SETAC Europe Annual Meeting*. Nantes, France. **TU218**.

Chapter 2 - Oil sludges: characteristics, sources and treatments

2.1. Introduction

The world petroleum production is about 12,600,000 $m^3 \cdot day^{-1}$ every year. The generation of oil sludges is approximately 190,000 m^3 per day (ANP, 2010). Oil sludges have no further use, and therefore these wastes are significant for the oil industry (Dibble and Bartha, 1979). However, the oil from the sludges is considered to be a valuable source of energy which can be reused as fuel (Shie *et al.*, 2000). In fact, oil sludges can have high levels of potential energy and a calorific value with an average of 5000 kcal·kg (Jiang *et al.*, 2012). For these reasons, the main objectives of the treatment and management of oil sludges are the **r**eduction, **r**e-utilisation, and **r**ecycling of these wastes. These targets are known as "*the 3R concept*" (Sakai *et al.*, 2011). Also, the Directive 2008/98/EC (European Community) addressed the importance of prevention, recovery, and reuse of waste oils (European Parliament, 2008). Therefore, most of the treatments aim to separate the extractable components of oil in the sludge for energy reuse (Wang *et al.*, 2010). Oil recovery using surfactants can be considered as a convenient and feasible process because this technique reduces high oil concentrations in the sludge and takes advantage of the recovered oil as fuel (Zhang *et al.*, 2012). Since the major component of the oil sludges is the crude oil itself which has a potential reuse, this thesis focuses on this component. The next section discusses more the characteristics of the crude oil.

2.2. Crude oil

The term petroleum includes both the crude oil and gas and their petroleum products obtained from the refining. The crude oil is the raw oil itself extracted from the underground reservoirs (England *et al.*, 1987). Carbon and hydrogen are the main elements found in the crude oil. There are also constituents known as NSO compounds (composed of nitrogen, sulfur, and oxygen) and heavy metals (e.g. nickel, vanadium, and iron) (Wang and Fingas, 2003). The oil compounds are known as petroleum hydrocarbons (PHCs).

Petroleum hydrocarbons (PHCs) are classified as aliphatics, aromatics, compounds with nitrogen, sulphur, and oxygen (NSO), and asphaltenes (Mrayyan and Battikhi, 2005; Reddy *et al.*, 2011). PHCs can be measured in terms of total petroleum hydrocarbons (TPHs) as mentioned by the Agency for Toxic Substances and Disease Registry (ATSDR, 1999b). TPHs are a broad group of the measurable amount of PHCs in a determined environmental matrix (e.g. crude oil, oil contaminated soil), and these compounds are divided into aliphatic and aromatic hydrocarbons. The TPH group includes several hundred different compounds. The aliphatic compounds include *n*-hexanes C_6, *n*-decanes C_{10}, *n*-dodecanes C_{12}, cyclohexanes, and higher molecular compounds such as tetracosane C_{24} and *n*-hexacosane C_{26}. The aromatic compounds comprise the polycyclic aromatic hydrocarbons (PAHs) along with the **b**enzene, **t**oluene, **e**thylbenzene, and **x**ylene (BTEX) isomers and phenols. PAHs with higher molecular weights such as benzo[a]pyrene or fluoranthene are considered to be carcinogenic (Kennish, 1996). Because a crude oil can have a high quantity of different PHCs, the total amount of these hydrocarbons is given as TPHs instead of the mass of each hydrocarbon. In fact, the amount of TPHs is used as a standard indicator of contamination with petroleum (ATSDR, 1999b).

TPHs are referred as the sum of the volatile petroleum hydrocarbons (VPHs) and the extractable petroleum hydrocarbons (EPHs). VPHs are divided into one aliphatic fraction of C_5-C_{12} compounds and one aromatic fraction (C_9-C_{10}). EPHs are referred to the C_9-C_{18} and C_{19}-C_{36} aliphatic fractions, and the aromatic fraction with C_{11}-C_{22} compounds [Texas Natural Resource Conservation Commission, TNRCC (2001); Massachusetts Department of Environmental Protection (2004)]. The measurement of oil concentrations is usually done in terms of EPHs due to the rapid volatilisation of lighter oil fractions (VPHs) (Heidarzadeh *et al.*, 2010; Okparanma and Mouazen, 2013). For instance, the EPHs concentrations are quantified using gas chromatography with a flame ionisation detector (GC-FID). This method measures the petroleum hydrocarbons based on the differentiation of the compounds by their boiling point distribution. Although the GC-FID cannot detect the higher volatile compounds (i.e. hydrocarbons compounds with less than six carbons such as butane and pentane), these compounds are not expected to be found in environmental samples because they have a high volatilisation level (USEPA, 2001).

Gas chromatograms (GC) are used to view and quantify the different oil hydrocarbon fractions in the petroleum. Figure 2.1 shows an example of a crude oil chromatogram. The intensity of the peaks, which is related to the concentration, decreases from light to heavier hydrocarbons; this is a general characteristic of the GC profile of crude oil. Also, this

chromatogram shows the distribution of the EPH aliphatic fractions (C_9-C_{18} and C_{19}-C_{36} hydrocarbons).

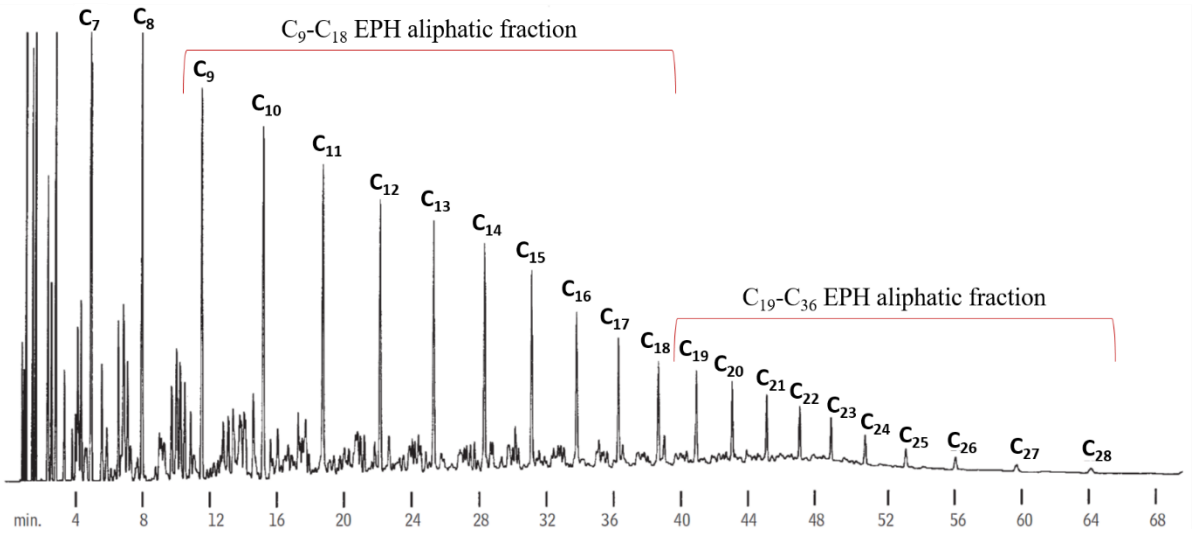

Figure 2.1. Gas chromatogram of an Arabian light crude oil modified from the original to indicate the C_9-C_{18} and C_{19}-C_{36} EPH aliphatic fractions. The C_n corresponds to the number of carbons in each *n*-alkane. The x-axis shows the retention time in minutes, and the y-axis shows the intensity response of the peaks. The chromatogram was taken from the Restek Searchable Chromatogram Library.

Figure 2.2 shows a biodegradation study of crude oil from Oklahoma, USA (Mansuy *et al.*, 1997).

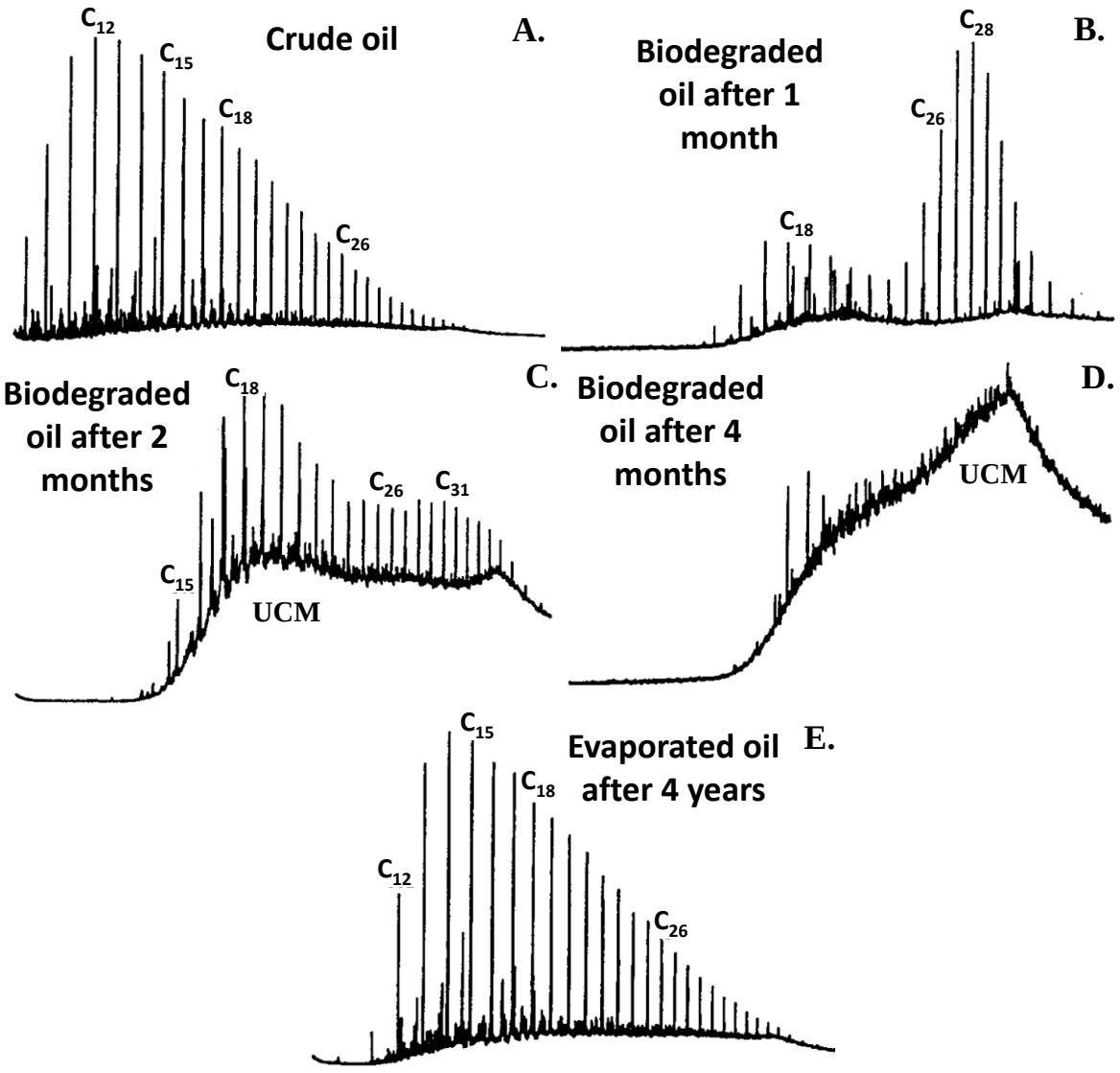

Figure 2.2. Gas chromatograms of the biodegradation with the addition of an activated sewage sludge to crude oil. The crude oil (A) came from Oklahoma. The chromatograms are from one month (B), two months (C), and four months (D) of biodegradation. A chromatogram of the oil after a 4-years evaporation period at room temperature is shown for comparison (E). The C_n corresponds to the number of carbons in each *n*-alkane. UCM: unresolved complex mixture. The x-axis shows the retention time in minutes, and the y-axis shows the intensity response of the peaks. The chromatograms were taken from Mansuy et al. (1997).

The GC profile of this crude oil (Figure 2.2A) is similar to the chromatogram from Figure 2.1. The crude oil has a higher concentration of low-molecular-weight alkanes (C_{12}-C_{15} compounds). This crude oil for the biodegradation study had an addition of activated sewage

sludge. The activated sludge is produced in the industrial and sewage wastewaters treatment plants. Bacteria and protozoans are inoculated in the process to aid in the degradation of the organic contaminant in these wastes (Günder, 2001). Therefore, some biodegradation studies add activated sewage sludge in the matrix to treat because it is expected that the microorganisms from the sludge can degrade several types of contaminants (Markiewicz *et al.*, 2014). The low-molecular-weight hydrocarbons less than C_{15} disappeared, and the concentration of the compounds higher than C_{26} increased after one month of biodegradation (Figure 2.2B). Then, after two months (Figure 2.2C), the biodegradation process was more evident because the concentration of the *n*-alkanes decreased (e.g. C_{18} and C_{26} compounds). However, the concentrations of low-molecular-weight compounds increased relative to the high-molecular weight hydrocarbons. These results were rather surprising because it was expected more degradation of the low-molecular-weight hydrocarbons. Also, this chromatogram has a broad and well-defined increase of the baseline known as the unresolved complex mixture (UCM) due to the degradation and weathering processes (Figure 2.2C). The characteristic shape of this region resembles a "hump" that includes saturated cyclic hydrocarbons, naphto-aromatic, and polar compounds. Since the oil is degraded, several compounds are formed generating this hump which is not fully resolved by the GC-FID. Therefore, the comprehensive two-dimensional gas chromatography (GC × GC) is used to solve and analyse the compounds in the UCM by using two connected columns (Frysinger *et al.*, 2003). The UCM is prominent in samples with long biodegradation periods. In fact, the chromatogram from Figure 2.2D shows an increase of the UCM after four months of biodegradation. Also, the peaks of the *n*-alkanes disappeared completely. Finally, a chromatogram of a four-year period of evaporation of the crude oil is shown for comparison (Figure 2.2E). The concentration of compounds less than C_{15} decreased compared to the original crude oil (Figure 2.2A) due to evaporation and volatilisation events. However, both chromatograms of the original (Figure 2.2A) and evaporated oil (Figure 2.2E) are very similar. Also, the impact of the biodegradation in the crude oil is evidenced even after one (Figure 2.2B) or two months (Figure 2.2C) of biodegradation compared with the evaporated crude oil in a four-year period (Figure 2.2E).

Figure 2.3 shows chromatograms of the bioremediation of soil contaminated with oil sludge from the study by Makadia et al. (2011).

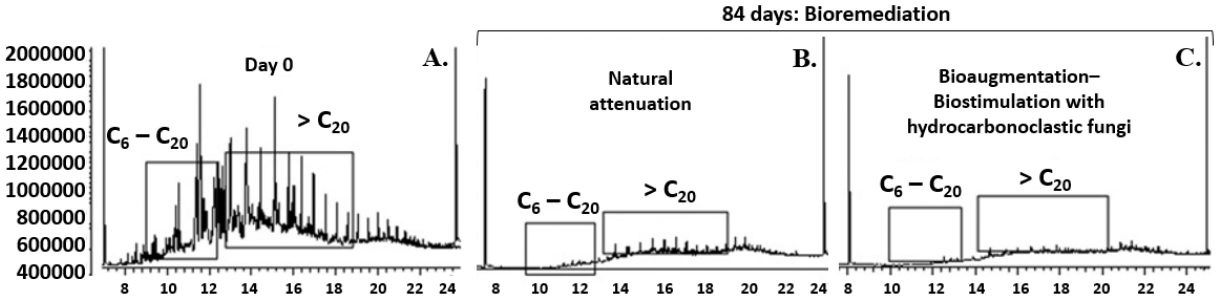

Figure 2.3. Gas chromatograms of soil contaminated with oil sludge at time zero (A) and after 84 days of bioremediation with natural attenuation (B) and with hydrocarbonoclastic fungi (C). The numbers C_n corresponds to the number of carbons in each *n*-alkane. The x-axis shows the retention time in minutes. The y-axis shows the intensity response of the peaks. The chromatograms were taken from Makadia et al. (2011).

The chromatogram at day zero (Figure 2.3A) shows high concentrations of the C_{20} hydrocarbons and some compounds with carbon numbers greater than 20 before the biodegradation study. After 84 days, when the contaminated soil was left under natural attenuation (i.e. degradation of oil hydrocarbons by native microorganisms and other physicochemical processes), the intensity of the peaks mentioned above decreased significantly (Figure 2.3B). However, if the contaminated soil is bioaugmented with an oil hydrocarbon degrader (i.e. hydrocarbonoclastic) fungus (*Scedosporium apiospermum*) and biostimulated with minimal media with nitrate, sulphate, and sulphate sources (Figure 2.3C), the peaks almost disappeared indicating a complete degradation. Even though the gas chromatograms with natural attenuation and with the hydrocarbonoclastic fungi are similar, the effect of the biodegradation was higher in the latter. This effect indicates the influence of the bioaugmentation event in the biodegradation process.

The crude oil processing, from extraction to the refining, consists of two types of operations (Figure 2.4). The crude oil extraction, transportation, and storing are included in the upstream operation, whereas the downstream operation is related to all the refining processes of the crude oil (Hu *et al.*, 2013). The sources of oil sludge in the upstream operation include the residual crude oil from the oil wells, drilling muds, and sludge accumulated at the bottom of oil storage tanks (O'Rourke and Connolly, 2003). Several sources can be found in the downstream operation including sludges from the oil/water separators, refined oil storage tanks, dissolved air flotation (DAF) units, and wastewater treatment plants (van Oudenhoven *et al.*, 1995). The

petroleum refining is the transformation of the raw material extracted in the drilling process into petroleum-based products such as petrol, liquefied petroleum gas (LPG), aviation kerosene, petroleum asphalt cement, and diesel (da Silva *et al.*, 2012). The oil refining process is explained in Figure 2.4. The refining begins with the fractionation of the raw oil in a process called atmospheric distillation. This fractionation occurred in a column where the crude oil is heated. Then, the oil is separated into several fractions which finally produced different oil derived products such as gasoline, kerosene and diesel. Residuals with heavy hydrocarbons distillates are treated in a second distillation called vacuum distillation (ANP, 2010).

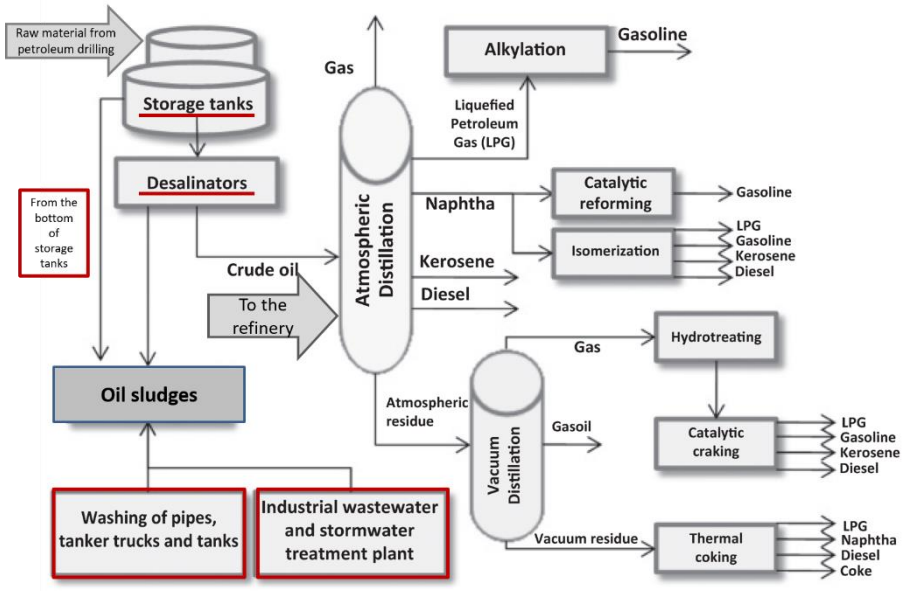

Figure 2.4. Petroleum refinery process with the sources of oil sludge. The most critical points are delineated in red. Adapted from da Silva et al. (2012).

2.3. Oil sludges

The petroleum industry can generate two types of oily wastes, the simple waste oils and oil sludges. The simple waste oils have a lower proportion of water and sediments compared to the sludge (Al-Futaisi *et al.*, 2007), whereas the oil sludge is composed mainly of oil hydrocarbons, water, and sediments. These sediments are formed from inorganic minerals in

drilling fluids, storage tanks, and rust and scale in the pipeline system (Giles, 2010). The water found in the oil sludge is usually from the refining and cracking processes of heavier hydrocarbons (Shailubhai, 1986), and may come with dissolved salts (Giles, 2010). The pH of the oil sludges can vary between 6.5 to 7.5 (Hu *et al.*, 2013). Moreover, oil sludges can be composed of polyethers (common chemical additives of refinery process), metals, and other chemicals generated in the petroleum refining process (Hu *et al.*, 2013). Zinc (Zn), chromium (Cr), vanadium (V), nickel (Ni), lead (Pb), and copper (Cu) are the main metallic elements found in the oil sludge. The main organic compounds include *n*-alkanes, paraffins, olefins, aromatics, asphaltics, phenols, and PAHs (Shailubhai, 1986). The metal content is much lower than the organic hydrocarbon content in the oil sludges. Oil sludges are considered hazardous wastes mainly due to the presence of PAHs and phenols that give their flammable state (Xia *et al.*, 2006). This waste is generated in the production, transportation, and storage of oil (Wang *et al.*, 2010; Zhang *et al.*, 2011b).

The heavy metals found in the oil sludges can come from the oil additives, the crude oil, and the oil extraction process (e.g. water and particles from the wells). These metals can cause fouling and poisoning of catalysts applied in the thermal cracking of heavy fractions of petroleum oil hydrocarbons (Elliot, 1996). V and Ni are originated from geological sources (Schirmacher *et al.*, 1993). Iron (Fe) compounds come from additives used as oxidation inhibitors (iron phosphides and sulphides). Zn is found in additive formulations (e.g. zinc dithiophosphates) which are employed in the oil industry as antioxidants and corrosion inhibitors. Also, Ca compounds such as calcium sulfonates are used in additives for corrosion prevention (Bartels *et al.*, 2000). Schirmacher et al. (1993) tested the concentrations levels of different metals in 34 crude oil and 29 oil sludge samples. They concluded that V and Ni are the most common elements in the crude oil, and Ca, Fe, and Zn are characteristic of the oil sludge. Moreover, Stigter et al. (2000) reported that the Cd, Cu and Zn elements in the crude oil come from external sources in the oil extraction such as the water and particles from the wells, whereas Cr is inherent in the crude oil. The main metal component of the oil sludge could be either calcium (Ca) or iron (Fe) (Schirmacher *et al.*, 1993). Also, sodium (Na) and Ni are found in the sludges, and these elements are known to be corrosive in the oil refining machinery (Abbas *et al.*, 2010). The American Petroleum Institute (API, 1989) mentioned some heavy metals concentrations in oily sludge from petroleum refineries. The ranges of concentrations for Cr can be between 30 and 80 ppm, for Cu from 30 to 120 ppm, for Ni from 15 to 25 ppm, and for Pb from 0.001 to 0.12 ppm.

Table 2.1 summarises the physicochemical characteristics of oil sludges with the most reported concentrations.

Table 2.1. Percentage ranges of the common components found in oil sludges.

Components	Percentage range [1]
Water	30 – 90
Sediments, solids [2]	4 – 7
Oil [3]	5 – 60
Aliphatic	*40 – 60*
Aromatic [4]	*25 – 40*
Resins	*10 – 15*
Asphaltenes	*10 – 15*

[1] Data reviewed by da Silva et al. (2012). Since these values are ranges, the values do not add up.
[2] According to Monteiro et al. (2007), most of the sediments are composed of calcite, halite, kaolinite, and quartz.
[3] These are the components found in the oil. Therefore, the percentage range values of the components only belong to the oil component. Data from Shie et al. (2004) and Speight (2006).
[4] The most common aromatics found are the BTEX compounds, phenols, and PAHs (Shie *et al.*, 2004).

In general, the crude oil from the sludges had a higher aliphatic fraction content (40 – 60%) compared to the aromatic content (25 – 40%) (Shie *et al.*, 2004; Speight, 2006). Data from several sources have identified the common ranges of water, solids and sediments, and oil in the oil sludge. The variation in these percentages depends on the origin of the oil sludge (Viana *et al.*, 2015). Therefore, there is no agreement among authors since the oil sludge composition is unique. For instance, da Silva et al. (2012) claimed that the composition of oil sludge is about 30 to 90% of water, 4 to 7% of sediments, 5 to 60% of the oil. However, Saikia et al. (2003) stated that the typical composition of oil sludge is 30-50% of water, 10-12% of sediments and solids, 30-50% of the oil. Yang et al. (2005), Zhang et al. (2012), and Long et al. (2013) have agreed that oil sludge is usually composed of 30-70% of water, 2 to 15% of sediments and solids, 30-90% of the oil. Despite the differences among authors, the percentage fraction of sediments and solids is usually less than the oil and water percentages. Also, these authors agreed that the oil sludge is composed of water-in-oil type (W/O) emulsions (i.e. water droplets dispersed in oil).

According to El-Batanoney (1999), the formation of W/O emulsions is influenced by the presence of asphaltenes, resins, fine solids, and oil-soluble organic acids. An emulsion is

the presence of droplets of an immiscible liquid (e.g. oil) dispersed into another immiscible liquid (e.g. water), which creates a stable suspension (Barnes and Gentle, 2005; Rosen and Kunjappu, 2012). An interfacial protective film contributes to this stability of the W/O emulsion in the sludge (Hu *et al.*, 2013). Emulsifying agents are required to form the emulsion between the two immiscible liquids by creating this interfacial film. In the case of the oil sludge, the emulsifying agents are the sediments contained in the sludge, and the asphaltenes and resins present in the crude oil (Yang *et al.*, 2009; Kralova *et al.*, 2011; Rosen and Kunjappu, 2012). This interfacial film has a high viscosity which surrounds the water droplets with their polar portions directed to the water and the non-polar parts to the oil (Rosen and Kunjappu, 2012). The degree of the emulsion strength is important in the oil sludge because this can contribute to the stability and the integrity of the oil sludge. Moreover, if the oil sludge has a strong and stable emulsion, it will require a method that can break the emulsion successfully. Then, the oil can be recovered, or the oil becomes bioavailable for a bioremediation process.

2.4. The critical points of oil sludge formation

According to Rahman et al. (2003), the main sources of the generation of oil sludges are oil storage tanks and oil-water separation systems; oil tank bottom sludges are the most studied sludges (Rahman *et al.*, 2003; Hu *et al.*, 2013). Most often, these sludges have a high viscosity, so their removal from the bottom of the tank is difficult (Lima *et al.*, 2011). The high viscosity can be attributed to the separation of heavier and lighter PHCs from the crude oil. This heavier fraction precipitates and mixes with the sediments and water at the bottom of the tank (Ayotamuno *et al.*, 2007).

Other sources included the oil sludge formation with waste engine oils from vehicles and machines. Lam et al. (2012) mentioned that about 24 million tonnes of waste automotive engine oil are generated every year in the world. The engine oil can have traces of lubricant which allows the reduction of friction and the heat generated by the machines (Mohammed *et al.*, 2013). After the engine or machine consume the oil, there can be some remnants of oil in the engine. This oil can be mixed with residuals from the engine such as sediments, metals, soot, and other corrosion and combustion products (Rahman *et al.*, 2008). Then, the waste engine oil can be polymerised along with the residuals due to the high temperatures from the engine. This event can contribute to the formation of sludges (Mohammed *et al.*, 2013).

Due to the different sources of oil sludges, these wastes are catalogued by the Review of the European List of Waste under the category of "*wastes from petroleum refining, natural gas purification and pyrolytic treatment of coal*" (Okopol, 2008). The sludges mentioned under this section included desalter, tank bottom, and oil sludges from the maintenance operations of the plant and equipment. In addition, the review had a section for "*oil wastes and wastes of liquid fuels*" where it is mentioned the waste from the engines, gear and lubricating oils and sludges from oil/water separators (Okopol, 2008). The International Petroleum Industry and Environmental Conservation Association (IPIECA) classified the oil sludges into four types depending on their contents as follows. First, oil sludges with detergents or washing liquids from the washing of the equipment used in the refinery process. Second, oil sludges containing grease and non-mineral skimmed foam from the effluent treatment stations, floaters, flocculators and water-oil separators. Third, light oily sediments with minerals obtained from desalinators, and fourth, heavy and oily sediments with minerals originated at the bottom of the storage tanks and from desalination (IPIECA, 2004).

2.5. Impact of the generation of oil sludges

The organic and inorganic co-contamination contributes to the toxicity of oil sludges. Therefore, it is important to treat these wastes effectively due to their potential threats in the environment (Hu *et al.*, 2013). In general, high molecular weight PAHs are catalogued as genotoxic to humans. This toxicity increases with higher molecular weight PAHs (Robertson *et al.*, 2007). Moreover, the recalcitrance of the PHCs can be intensified during weathering of oil sludges, and therefore, the aged oil sludge becomes more chemically stable decreasing its availability to be degraded (Tang *et al.*, 2012). Heavy metals from oil sludges cannot be degraded into less hazardous chemical species as the organic contaminants. However, these inorganic contaminants can be transformed from their toxic states into less toxic and stable immobile forms (Uhrie *et al.*, 1996; Beyenal and Lewandowski, 2004). These heavy metals are included in the group of potentially toxic elements (PTEs) when they higher than the tolerable levels for organisms. PTEs can be found in soils naturally at low concentrations, and some of these such as Zn, Cu, and Ni are required in the metabolism of the organisms. As mentioned before, the heavy metals found in the oil sludges can originated from the oil additives added in

the oil extraction and refining processes (de Souza *et al.*, 2014), and therefore, they can become potentially toxic.

Besides its impacts on the environment, the formation of oil sludges can also affect the petroleum industry negatively. The stable W/O microemulsions in oil sludges are one of the most common sources of operational problems (e.g. clogging) in the oil industry (Del Carpio *et al.*, 2014). Additionally, the presence of water in the oil industry and oil sludges can corrode the equipment used, and it can decrease the American Petroleum Institute gravity (API) gravity of the oil, affecting its quality (Del Carpio *et al.*, 2014).

This thesis focuses on the oil recovery from oil sludges by washing with surfactants and co-solvents, and there is no immediate hazard or negative impact as this process is performed in a closed system. The possible hazard or toxicological impact can be found in the residual sludge from the oil sludge washing process. If these residuals are disposed of, some concentration of contaminant (organic and inorganic) can still be present. Therefore, the residuals have to be treated with alternative techniques such as landfilling or bioremediation methods. For example, in landfarming, the residuals can be added to a specific area as an amendment to the soil (See Section 1.1). Furthermore, plants can be planted in this area for a phytoremediation process. Due to the possible accumulation of contaminants in the plants during the phytoremediation, the plants cannot be used for food consumption. Therefore, soybeans can be used to have an economic advantage for the production of biodiesel as mentioned before. If this area is isolated in a closed system with impermeable layers, the risk of leachates can decrease substantially. Likewise, if the oil recovery process evaluated in this study is applied at a large scale, it has to be ensured that a closed system is designed with tanks and pipes properly sealed.

2.6. Treatment of oil sludges

In general, the current strategies to treat oil sludges are divided into two groups, the physicochemical (Section 2.6.1) and the biological methods (Section 2.6.2). Among the physicochemical methods, three subgroups are classified depending on the aim of the method. If the objective is to dispose directly of the oil sludge, landfilling is used. The second subgroup consists in the reduction or elimination of the oil sludge, and the methods include incineration,

oxidation, and encapsulation. The last subgroup includes methods to recover the oil from the sludge, so it can be reused. In this case, the methods are centrifugation, pyrolysis, electro-demulsification, microwave or ultrasonic irradiation, freeze/thaw, solvent extraction, froth flotation, and surfactant enhanced oil recovery (EOR). On the other side, the main objective of the group of the biological methods is to reduce or eliminate the burden of the organic or inorganic contaminants in the sludge. Therefore, bioremediation techniques such as landfarming, biopiles and bioreactors with microorganisms, and phytoremediation with plants are used.

2.6.1. Physicochemical methods

Landfilling is a method in which the oil sludge is disposed of in a designated area without further treatment. One risk associated is the secondary pollution by the production of gas and leachate with strong odours that includes heavy metals and organic contaminants. Landfilling is the option when the waste cannot be reused or recycled (Verma, 2009). However, sometimes the disposal of this hazardous sludge is contained within impermeable layers (Baheri and Meysami, 2002; da Silva *et al.*, 2012). This technique is called secure landfilling, and it uses leachate collectors (Moses *et al.*, 2003). Secure landfilling is often applied in the UK, Germany and North America, but the costs of secure landfilling are high due to the materials needed to ensure a complete isolation of the landfill area (Bhattacharyya and Shekdar, 2003). This technique does not treat or decontaminate the sludges, so other methods are applied to reduce or eliminate the volume of sludge. Landfilling can be useful to dispose of the residual material obtained from other treatment of oil sludges as it is expected that the contaminant burden will be below the established waste acceptance limits at the landfills. For example, the UK Environment Agency established that the limit of total organic carbon (TOC) in the hazardous waste to landfill is 6% (w/w). For heavy metals such as Cd, Cr, Cu, Ni, and Pb, the limit levels are 5, 70, 100, 40, 50 $mg \cdot kg^{-1}$, respectively (UK Environment Agency, 2013). Landfilling is the least expensive of the physicochemical methods, as the cost of disposal can be around 80 – 160 $GBP \cdot ton^{-1}$ of oil sludge-contaminated soil (Mater *et al.*, 2006).

Incineration consists of the use of thermal decomposition at higher temperatures in furnaces to reduce or eliminate the volume of oil sludge. Also, this method needs air in excess and auxiliary fuels (e.g. fuel oil and propane) to ensure its success (EC, 2006; da Silva *et al.*,

2012). In fact, the use of excessive air and oxygen supplies in the incineration is the main difference with pyrolysis as this method is performed in an inert ambient with N_2. The temperatures used can variate between 750 to 1,200°C depending on the incinerator used (Hu *et al.*, 2013). Moreover, it was reported that setting the temperatures between 1,100 and 1,400°C is better than temperatures between 850 and 900°C because all organic content from the sludge is incinerated and the residual ash content can be less than 1% at these temperatures higher than 1,000°C (EC, 2006). Although this method aims to reduce and eliminate the volume of oil sludge, some energy that is produced after the incineration can be recovered in the form of steam which can be used for electricity generation (Sankaran *et al.*, 1998). Incineration is considered to be efficient for converting most of the organic compounds in the sludge into CO_2 and water. For instance, in a study by Sankaran et al. (1998), the combustion efficiency of the sludge varied with the amount of water present in the sludge. Therefore, the combustion efficiency was 99% with a low water content, but it was 51% with a higher water content. In this case, more auxiliary fuel is needed to improve the combustion efficiency and to overcome the high presence of moisture in the sludge (Sankaran *et al.*, 1998). Some problems of the method are the excessive temperatures, air pollution for gas emissions generally by incomplete combustion, and clinker formation. Also, some drawbacks of the incineration method are the production of carcinogenic compounds (PAHs, sulphur and nitrogen oxides, dioxins, and BTEX) and the presence of heavy metals in the residual ash (Chang *et al.*, 2000; Bhattacharyya and Shekdar, 2003; Al-Futaisi *et al.*, 2007). Moreover, the operating costs at large scale are high in terms of the adaptation of a proper furnace that can contain the heat for more time, and the need for additional fuels and constant air supply (EC, 2006). The costs can also increase for oil sludges with high viscosity levels or high water contents, so a pretreatment has to be applied to reduce these levels (Sankaran *et al.*, 1998). In fact, the incineration expenses can be around 650 $GBP \cdot ton^{-1}$ of incinerated oil sludge (Habibi, 2004).

Oxidation processes can decrease the organic contaminant burden in the oil sludge. The ***oxidation treatment*** consists in the use of chemicals to either oxidise the organic compounds to carbon dioxide and water or to transform the sludge into inorganic salts. The chemical oxidisers include ozone, Fenton's reagent (hydrogen peroxide and ferrous iron solution), permanganate, and hydrogen peroxide (Ferrarese *et al.*, 2008). The Fenton oxidation reaction generates hydroxyl radicals ($OH^{\cdot}$) that react with organic and inorganic compounds (Bianco *et al.*, 2011). Moreover, the generation of the $OH^{\cdot}$ radicals can be advantageous when treating oil sludges with a high concentration of PAHs as these radicals are very reactive with these

aromatic compounds (Keyte *et al.*, 2013). Therefore, this method was applied with promising results in the degradation of PAHs and BTEXs in soils contaminated with oil sludges during an 80 hours-oxidation treatment process with the Fenton's reagent. In fact, the PAH and BTEX total reductions were 94% for both groups of hydrocarbons (Mater *et al.*, 2006). Also, da Rocha et al. (2010) reported a 99% PAHs removal from a tank bottom oil sludge in a 96 hours-oxidation study. An advantage of this treatment is that it does not depend on factors such as temperature change and pollutant loading (Hu *et al.*, 2013). Also, the oxidised compounds had a higher biodegradability compared to the untreated sludge (Jing *et al.*, 2011). Some authors have used this method in combination with bioremediation techniques (Section 2.6.2) such as landfarming of matrices contaminated with high PAHs concentrations, as the oxidation can enhance the biodegradation of these compounds (Nam *et al.*, 2001; Haapea and Tuhkanen, 2006; Kulik *et al.*, 2006). In fact, after the combination of the Fenton oxidation and bioremediation in contaminated soils, the amount of PAHs with 2- and 3-rings and 4- and 5-rings reduced by a 98% and 85%, respectively (Nam *et al.*, 2001). However, when the treatment was only the Fenton oxidation, the reduction was 80% for the 2- and 3 -rings PAHs and 20-40% for the 4- and 5-rings PAHs. Farzadkia et al. (2014) mentioned that the maximum TPH reduction rate was 36% in a Fenton oxidation process of a tank bottom oil sludge for 1 hour. Interestingly, the TPH reduction rate improved to 73% by adding 40 ml of water per gram of oil sludge. Also, these authors proposed that the Fenton oxidation process is a pretreatment of oil sludges because the levels are often not reduced to the acceptable standard limits to dispose of the sludge. Therefore, it is necessary to apply another method to treat the sludges further. Similar to other techniques, this method is limited when large amounts of oil sludges are treated because this implies more costs for the process and the equipment needed (Hu *et al.*, 2013). However, the equipment used is easy to operate compared to other treatments such as incineration (Diya'uddeen *et al.*, 2015). Since the oxidation treatment does not need heating, the energy consumption and costs can reduce. Rivas et al. (2001) reported that the use of the Fenton oxidation in the treatment of wastewater from olive mills can cost about 3 GBP$\cdot m^3$ of wastewater. However, this cost is greater than the biological treatment applied to the wastewater by one order of magnitude due to the costs of the hydrogen peroxide. For instance, the cost of one tonne of a 50% solution of hydrogen peroxide can be approximately 250 GBP (Rivas *et al.*, 2001). To date, the oxidation process is still at a laboratory scale phase, so there a no records about the costs of this treatment in oil sludges.

Encapsulation involves ***solidification and stabilisation*** of the contaminants (Ball *et al.*, 2012). Stabilisation refers to the transformation of the contaminants into less soluble and toxic forms, and solidification focuses on the production of a solid mass of the sludge (Ball *et al.*, 2012; Hu *et al.*, 2013). An application of encapsulation is the ***oil sludge incorporation and stabilisation in ceramic materials***. For example, this technique is useful in the fabrication of ceramic or cement blocks (da Silva *et al.*, 2012). However, there is some uncertainty in the stability of these wastes in the ceramic materials due to some properties and composition changes influenced by the weathering of hydrocarbons, volatilisation of contaminants, oxidation and resinification of the crude oil (Mansurov *et al.*, 2001). In addition, Monteiro et al. (2007) found some chemical modifications of the ceramic material due to the addition of oil sludges. However, if the ceramic blocks are prepared using about 10 to 20% of oil sludge in weight, the blocks can be chemically stable. This requirement limits the possibility to treat large quantities of oil sludges. An advantage of this technique is that it is an alternative to treating heavy metals present in the oil sludge by their immobilisation at the stabilisation step. In fact, Karamalidis and Voudrias (2007) reported that around 98% of heavy metals was immobilised in the ceramic blocks. However, some leaching from the can be generated from the obtained solid mass (Hu *et al.*, 2013). According to Ball et al. (2012), the solidification/stabilisation costs can be between 50 – 150 GBP·ton^{-1} of oil sludge. Although these expenses are relatively high, it is possible to obtain a profit with the production of ceramic blocks. For example, the total profit from the production of one tonne (1,000 kg) of concrete blocks with 15% (w/w) of treated oil sludge is approximately 250 GBP. In this case, the amount of stabilised/solidified oil sludge used for producing one tonne of blocks is 150 kg (Mater *et al.*, 2006). Considering that a commercial ceramic block weighs approximately 20 kg, about 50 ceramic blocks can be obtained from one tonne. Indeed, the profit gained by commercialising these ceramic blocks can compensate the operational costs of the solidification/stabilisation of the oil sludge.

There are other methods which aim to extract the oil from the sludges. The ***oil recovery methods*** are based on the premise of recycling the oil from the oil sludge. In fact, it has been suggested to try this approach to treat the oil sludges as mentioned before (European Parliament, 2008; Sakai *et al.*, 2011). The following are the oil recovery methods used to treat oil sludges.

Centrifugation aims to recover the oil from the sludge by the separation of solid and aqueous phases. Therefore, the bottom layer is the sediment with the sludge and the heavy oil

hydrocarbons, and the top layer is a light hydrocarbon-containing liquid supernatant (da Silva *et al.*, 2012; Hu *et al.*, 2013). This supernatant is further separated in a liquid/liquid phase reaction to obtain the light hydrocarbons (Corti and Falcon, 1989). It has to be noted that this technique does not allow the recovery of heavier oil contents from the sludge. In fact, some quantity of oil content (5-10 wt%) can remain in the sediment after centrifugation (Japan External Trade Organization (JETRO) *et al.*, 2010). In fact, it is necessary to pretreat high-viscosity oil sludges with organic solvents, surfactants, or other demulsifying agents to reduce the viscosity before the centrifugation (Cambiella *et al.*, 2006; Zubaidy and Abouelnasr, 2010). Therefore, this method is not efficient when applied alone. For instance, it was reported that the addition of calcium chloride ($CaCl_2$), a coagulant salt, improved the centrifugation by obtaining an oil separation efficiency of 96% (Cambiella *et al.*, 2006). This process has relatively low costs at lab scale (da Silva *et al.*, 2012). However, the disadvantages of this method are the high costs of the centrifuge and the high energy demands at a large scale application (Nii *et al.*, 2009), including the additional pretreatment of the sludges to reduce the viscosity. Therefore, the large scale application of the centrifugation includes a pretreatment tank to decrease the viscosity of sludge. Since the separated water can still have some PHCs, these residuals are treated in an oil wastewater treatment plant (Hu *et al.*, 2013). No reports were found about the costs of centrifugation of oil sludge at a large scale.

Pyrolysis, also known as destructive distillation and thermal oxidation, is a process involved in the conversion of oil sludge into volatile light organic compounds and CO_2 using a thermal reactor (da Silva *et al.*, 2012). Even though pyrolysis converts and reduces the oil sludge to light organic compounds and CO_2, this technique can also be considered as an oil recovery method. Specifically, the products formed by the pyrolysis reaction are N_2 (from carrier gas) and from the highest to the lowest percentage, carbon dioxide, hydrocarbons (C_1-C_2 paraffins and olefins), water, and CO_2. However, since this is an endothermic process that burns the sludge in a similar way as the incineration, pyrolysis can generate some residue such as char (Fonts *et al.*, 2012). One difference with incineration is that these recovered volatile petroleum hydrocarbons compounds (VPHs) can be cooled down and transformed into a liquid state (Liu *et al.*, 2011). The condensable volatile fractions (i.e. hydrophilic solutions and water) are recovered using a glass condenser into a liquid state. For the recovery of the oil or non-condensable volatile gases, these compounds are passed throughout a glass ampule with water. Then, the gases displace the water, and they are collected in gas bags. After heating up to about 150 °C and centrifuging the condensate, the oil can be separated and recovered from the water

phase (Wang *et al.*, 2007). The recovered liquid can be used as a feedstock for fuel production (Liu *et al.*, 2011). For instance, it can have distillation characteristics similar to diesel oil (C_8-C_{24}) (Chang *et al.*, 2000). Another difference with incineration is that this process is undertaken in an inert environment using a constant flow of N_2 to ensure the purge of the air flow. The temperature of this reaction ranges between 500 and 1,000 °C (Hu *et al.*, 2013), but it can be lower compared to incineration (Wang *et al.*, 2007). Chang et al. (2000) reported that the products obtained after a pyrolysis of sludge from an oil storage tank were CO_2 (51 wt %), PHCs (25 wt %), water (18 wt %), and CO (6 wt %). Also, the oil sludge can be reduced to about 10 or 20% of its original volume (Wei and Wu, 1997). Schmidt and Kaminsky (2001) reported oil recovery rates between 70 and 84 wt % from an oil sludge by using pyrolysis (460-650 °C) in a fluidised bed reactor. Moreover, this process can improve by using additives such as sodium and potassium. In fact, the addition of potassium chloride (KCl) improved the oil recovery rate from an oil tank bottom sludge to 73% compared with the no-addition treatment (66%). The oil recovery rates with other additives such as potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), sodium chloride (NaCl), and potassium hydroxide (KOH) were 61%, 72% 66%, and 60%, respectively (Shie *et al.*, 2003). In another study, Shie et al. (2004) found that the initial oil sludge mass reduced by 40% with pyrolysis. The disadvantages of pyrolysis include the challenging large-scale application due to the high amount of energy required and the complexity of the oil recovery related to the successive condensation and heating processes (Li *et al.*, 2011). Also, it requires a previous step of dewatering to improve the pyrolytic process (Bridle and Unkovich, 2002). Moreover, the pyrolytic products can have some presence of PAHs (Chang *et al.*, 2000). Since this treatment has the advantage to condense the pyrolytic gas product with hydrocarbons and recover it into a liquid state, pyrolysis can be more convenient to use than incineration. To date, there are no reports on the costs of the pyrolysis treatment of oil sludges.

Electro-demulsification, also known as the electrokinetic method, consists in the application of a low electrical potential (10 V – 100 V) in a cell with an anode and a cathode to achieve the demulsification and further separation of the different phases (water, hydrocarbons, and solids) in the oil sludge (Elektorowicz *et al.*, 2006). A study found that the electrokinetic treatment can remove about 43% of light hydrocarbons and 63% of water from the oil sludge (Elektorowicz and Habibi, 2005). In fact, this enhanced de-watering effect by the electro-demulsification was reported by Yang et al. (2005). These authors reported a dewatering efficiency of 56.3% at a bench scale using a 4 cm cell and around 40% at a large

scale in a 15 cm cell. Also, Elektorowicz and Habibi (2005) mentioned that the removal of the light hydrocarbon content was improved to 50% by adding an amphoteric surfactant (e.g. a surfactant with both anionic and cationic centres). This method does not require quantities of energy as higher as the energy required by centrifugation and pyrolysis. This method is still at lab-scale application, and therefore there is a need to perform more studies on its application at industrial scale to know the oil recovery efficiency and costs involved (Hu *et al.*, 2013). Regarding this, it was proposed by Yang et al. (2005) that the pools for oil sludge storage can be used directly as the cell for the electro-demulsification. Indeed, the use of this pools can reduce the costs of transport and construction of a large container to hold the oil sludge to treat.

Microwave irradiation focuses on the separation of water from the oil sludges using microwave energy that causes the demulsification (Sandroni and Smith, 2002; Robinson *et al.*, 2008). The reduction of the viscosity by the microwave irradiation leads to the breaking of the emulsion and the settling of water droplets from the emulsion (Tan *et al.*, 2007). According to Xia et al. (2003) and Mutyala et al. (2010), this technology has a higher efficiency in the separation of water compared to gravitational sedimentation and common heating techniques mentioned before. There is a potential to apply this technique to sludges since it was found that the demulsification efficiency was close to 100% in an emulsion prepared in the laboratory (Xia *et al.*, 2003). However, it has to be considered that this prepared emulsion could not represent the complexity of the emulsions due to the presence of asphaltenes and oil additives and the weathering of the oil sludge that could increase the strength of the emulsion in a real case scenario (See Section 2.3). Moreover, Abdulbari et al. (2011) reported that the addition of surfactants (SDS, Triton X-100, and sorbitan monooleate) to the microwave irradiation helped to remove more than 90% of water from the emulsion. Microwave irradiation is a relatively rapid method (e.g. 15 to 30 minutes to achieve the demulsification) compared to other heating methods because the microwave energy has direct access through the sludge via the molecular interaction with the electromagnetic field. On the contrary, in the other heating methods the heating of the surface of the sample is applied by conduction, radiation or convection which requires more time (Tan *et al.*, 2007). In fact, Mudhoo and Sharma (2011) mentioned that the microwave irradiation is more efficient in applying the energy than other heating methods such as incineration or pyrolysis because there are lower thermal losses in the process of energy transfer due to the above mentioned direct contact with the sludge. Since oil sludges contain W/O emulsions, the microwave irradiation goes directly to the inner water phase which absorbs more energy compared to the oily phase. Then, the water phase expands due to this radiation,

so there is a pressure that makes the W/O interfacial film thinner. Consequently, the demulsification of the sludge occurs (Tan *et al.*, 2007). The energy requirements of the microwave irradiation are higher compared to the other heating methods because it is needed more energy to reach this direct contact (500 – 1000 W). However, the generation of hazardous emissions is reduced compared to the other heating methods (Mudhoo and Sharma, 2011). Tan et al. (2007) mentioned that another disadvantage is that the quality of the recovered oil can be compromised as this phase can have a considerable amount of water left; especially when the W/O emulsion is very strong. Moreover, its implementation can be relatively expensive at large scales due to the special equipment needed to reach the energy requirements (Hu *et al.*, 2013), and the application of a post-treatment method to reduce the water content in the recovered oil. There are no recent reports about the application of the microwave irradiation at a large scale. However, Fang et al. (1988) reported a microwave irradiation treatment at the field scale. In this case, approximately 50 kg of oil sludge were treated in a tank of 3 m high and 3 m in diameter. A microwave generator was connected to the tank, and four thermocouples were placed at different levels of the tank to test the temperature continuously. The oil recovery rate was 53% at 20 kW for 20 minutes.

Also, the ***ultrasonic irradiation*** method aims to destabilise the W/O emulsion and separate the solid and liquid parts of the oil sludge (Kim and Wang, 2003; Ye *et al.*, 2008). The violent collisions among particles increase the temperatures in the sludge matrix occasioning a decrease in the viscosity, which leads later to the break of the emulsion (Chung and Kamon, 2005). An additional advantage of this collision is that the solvents added to process can have easy access to the sludge matrix to recover the oil from inaccessible areas (Feng and Aldrich, 2000). When an ultrasonic treatment (frequency 28 kHz) was applied to a wastewater sludge, the oil separation rate was 56% (Xu *et al.*, 2009). Another study with the same frequency had a high oil recovery rate of 95% from an oil tank bottom sludge (Jin *et al.*, 2012). Regarding the advantages, this technique has a high efficiency in the oil recovery with no secondary pollution, and the duration is similar to the microwave irradiation treatment. On the contrary, it is very limited to be applied at a field scale due to the special equipment requirements (Hu *et al.*, 2013). In fact, more studies are needed to test the performance at an industrial scale. In fact, Canselier et al. (2002) mentioned that the ultrasonic intensity could decrease in a large ultrasonic tank, and consequently this can affect the oil recovery rate. Regarding the ultrasonic frequency, it was reported that it is better to have a lower frequency as this will favour the cavitation or formation of bubbles in the matrix which are crucial in the collision (Xu *et al.*, 2009). This

cavitation phenomenon is the responsible for the destabilisation of the W/O emulsion which is related to the increase and decrease of temperature and viscosity, respectively, and the enhancement of mass transfer in the liquid phase (Chung and Kamon, 2005).

A dewatering method known as ***freeze/thaw treatment*** is based on the removal of water by separating the oil and water in the breaking of the W/O emulsion or demulsification (Hu *et al.*, 2013). Freezing temperatures can range from -20 to -40°C (Lai *et al.*, 2004). The freezing and thawing events allow this separation due to volume expansion of the frozen water droplets and the further coalescence of these droplets (more details are discussed later in Section 2.11 and Figure 2.8). Briefly, as the temperature continue to decrease, the oil freezes. During the thawing process, the oil phase starts to coalesce, which leads finally to the separation of two separated bulk phases of the oil and water by gravity (Lin *et al.*, 2008). This method was used for the removal of water from a used lubricating oil refinery sludge. The W/O emulsion was strong in this sludge, and the water content was about 77 wt %. The freezing and thawing treatments were set at -40°C and 20°C (ambient temperature), respectively, and the water removal was about 90% (Chen and He, 2003). These authors mentioned that 6 hours of freezing were necessary to ensure a complete freezing. In fact, a plateau is reached at this point, and the dewatering ratio remained stable even after 30 hours. Also, Chen and He (2003) mentioned that a slow thawing process (20°C) enhanced the water removal particularly for samples with low water content, but there were no significant differences in the water removal for samples with a high water content. However, it was found in another study that a rapid thawing by microwave heating can enhance the demulsification. For instance, Yang et al. (2009) reported that the dewatering removal was 90% (v/v) using microwave heating in the thawing process compared to air (85%) and water bath thawing (80%) which were slower. Lin et al. (2007) reported that dry ice was a better freezing method (dewatering removal, 70%) compared to the use of a freezer at -30°C (20%), cryogenic bath (65%), and liquid nitrogen (10%). Therefore, both dry ice and cryogenic bath are more efficient as freezing methods compared to the slow freezing in a refrigerator and fast freezing using liquid nitrogen (Lin *et al.*, 2007). In this case, the W/O emulsion used had a 60% of water content for this study. Since the operational costs and the time invested in freezing and thawing are considered to be limitations (Jean and Lee, 1999; Jean *et al.*, 2001), the application of this method can be affected at a large scale. Indeed, the freeze/thaw treatment can be applied at large scale mostly in cold regions where the natural freezing favours the process (Hu *et al.*, 2013). On the contrary, the dry ice or cryogenic bath seems to be an alternative in warmer zones. In fact, Jean et al. (2001) suggested that the dry ice

can be added at the bottom of a freezing chamber and then, the oil sludge is poured into the chamber at an approximately 3:1 sludge to dry ice (w/w) ratio. To date, little is know about a solid application of the freeze/thaw method at an industrial scale.

Solvent extraction is based on the idea that organic solvents extract the oil (*"like dissolves like"* principle), and the remaining sludge with water and solids are separated in another phase. Then, a distillation device further separates the oil/solvent mixture (Al-Zahrani and Putra, 2013). A comparison study with different solvents showed that kerosene and naphtha cut (84%) and toluene (76%) had higher recovery rates of PHCs from solid oil sludges compared to other solvents including methylene (72%) and ethylene chlorides (70%), *n*-heptane (72%), and diethyl ether (70%) (El Naggar *et al.*, 2010). Taiwo and Otolorin (2009) reported that hexane and xylene recovered about 67% of PHCs from oil sludge. Also, the oil recovery improves by increasing the solvent to sludge ratio. In fact, a 4:1 ratio was optimal to recover about 39% and 32% of oil using methyl ethyl ketone (MEK) and LPG condensate, respectively. The oil recovery was 24% and 13% for MEK and LPG condensate at 1:1 solvent to oil sludge ratio, respectively (Zubaidy and Abouelnasr, 2010). Therefore, high solvent to oil sludge ratios are also beneficial because the amount of ash and high molecular weight compounds such as asphalts (C_{24}-C_{56}) and oil waxes (C_{20}-C_{50}) decreases. These heavier compounds are not necessary for the reuse as fuel because most of the fuel such as diesel and gasoline have lighter hydrocarbon compounds with C_5-C_{12} and C_8-C_{24}, respectively (Zubaidy and Abouelnasr, 2010). Also, the temperature can influence the oil recovery process with solvents. In fact, the higher the temperatures, the faster the process. However, most of the light PHCs fractions (C_{10}-C_{18}) evaporate compromising the quality of the oil. Conversely, if the temperatures are low, the efficiency of the oil recovery is compromised (Fisher *et al.*, 1997) as more time is needed to recover the oil. In summary, the use of solvent extraction is a fast and efficient method to separate the oil due to the "like dissolves like" feature of the organic solvents. In addition, solvent extraction can treat a high amount of oil sludge (Hu *et al.*, 2013). However, costs can increase since the solvent extraction needs heating for solvent recycling purposes. Also, the application of this method at large scale implies the use of higher volumes of solvent. Even though one environmental concern is the potential hazard of the VOCs released by the solvents to the environment and the human health (Hu *et al.*, 2013), a closed system is used to avoid this situation. In fact, AERCO (1995) proposed a large-scale system which consists of a closed and continuous system (Figure 2.5). First, the oil sludge is mixed into a reactor column with the solvent. Although the authors did not mention, the reactor can

have an agitator to ensure a proper mix between the oil sludge and the solvent. Then, three layers are obtained. A bottom layer of the sludge sediments, a middle layer with the water from the sludge and other hydrophilic compounds, and a top layer of the oil and solvent. The oil and solvent mixture is transferred to a distillation system which separates and recover the oil and the solvent vapour. A compressor and cooling systems liquefy this vapour, and it is recovered in a solvent recycling tank. Therefore, the solvent can be reused in another cycle of solvent extraction. Alternatively, a second distillation system separates some solvent that can still be adsorbed at the sediment phase. Finally, the residuals obtained from the process are treated using other methods such as landfarming, if necessary, as mentioned before.

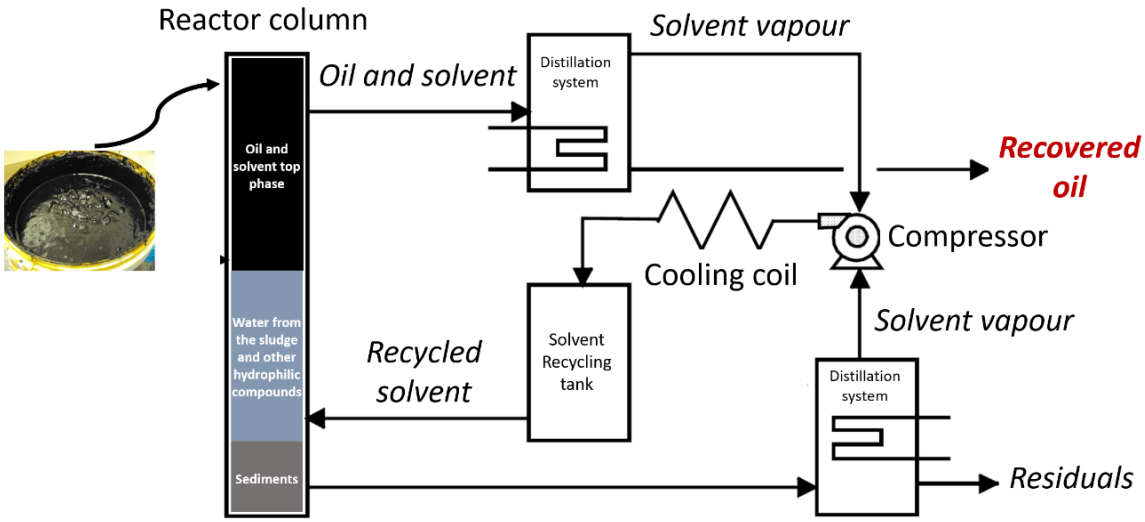

Figure 2.5. Diagram of a solvent extraction system proposed for a large scale scenario by AERCO (1995). The picture was modified from the original.

Froth flotation is based on the separation of solid particles from a liquid suspension which is stirred at a constant speed in a flotation cell (Ramaswamy *et al.*, 2007). After, there is a formation of air bubbles in the aqueous matrix, and these bubbles sequestered the oil droplets and fine solids. Then, the bubbles levitate to the froth layer by the increase of buoyancy (Urbina, 2003). When microbubbles (< 100 µm) are used, the process is known as dissolved

air flotation (DAF). In this case, the microbubbles are formed in two steps (Al-Shamrani *et al.*, 2002). First, the air is dissolved using a saturator set at high pressures between 400 to 600 kPa (Edzwald *et al.*, 1992). Then, these types of bubbles are formed when the water is poured into the flotation cell at atmospheric pressure. The use of microbubbles can enhance the flotation process because these bubbles have less rising velocity and higher surface area compared to the larger bubbles. Therefore, these events allow longer residence times in the cell to ensure more collisions between the bubbles and the sludges particles (Al-Shamrani *et al.*, 2002). For example, Ramaswamy et al. (2007) evaluated the oil recovery from oil sludge prepared in the lab using a synthetic anionic surfactant, sodium dodecyl benzene sulphonic acid (SDBS), in a froth flotation process. The maximum oil recovery (60%) from the oil sludge was achieved with the highest amount of surfactant used (20 g) and a flotation time of 12 minutes. Although this method is less expensive compared with the treatments mentioned previously, froth flotation is limited to sludges with low viscosity. However, temperatures can be increased during the treatment to enhance the reduction of viscosity in the sludge (Al-Otoom *et al.*, 2010). Furthermore, the recovered oil layer has a considerable amount of moisture and solids, so a post-treatment is needed to purify this layer. Another disadvantage is that the froth-flotation treatment is not effective in achieving the desorption of oil contained in the sediments from the sludge. Moreover, this method is limited to oil sludge with low water content, so a large volume of water is needed to generate the liquid suspension that favours the flotation (Hu *et al.*, 2013). The froth-flotation is still at a laboratory scale phase, and more studies are needed to test the performance at a large scale.

Until now, this literature review mentioned the use of surfactants to improve the oil recovery in different methods such as centrifugation, electro-demulsification, microwave irradiation, and froth flotation. Therefore, the surfactant itself can be used as a main component in an oil recovery separated method.

For instance, ***Surfactant Enhanced Oil Recovery (EOR)*** have been used to treat oil sludges by washing the sludges with surfactant solutions. In general, EOR, also known as tertiary oil recovery is referred in the petroleum industry as the last third stage of oil recovery when the oil is extracted using external fluids such as surfactants. The other two phases are known as primary oil recovery in which the oil comes naturally to the surface in the oil drilling without the injection of external fluids, and the secondary oil recovery in which the injection

of water and gas enhances the recovery (Sheng, 2011). Surfactant EOR is based on the premise that the solubilisation of oil into the surfactant micelles is one of the mechanisms of removal and recovery of oil. In this case, the amphiphilic nature of the surfactant creates micelles as the result of agglomeration of surfactant monomers. Each micelle has an outer hydrophilic part dissolved in polar liquids, generally water, and the inner hydrophobic part in the micelle core entraps and recovers the oil (Hu *et al.*, 2013). Specifically, Cheah et al. (1998) mentioned that the oil recovery depends on the concentration of the surfactant. When the surfactant is below its critical micelle concentration (CMC) (i.e. this is the concentration at where micelles can be detected) and no micelles are present, it can mobilise the organic contaminant by the reduction of the interfacial tension and capillary forces. On the other hand, when the surfactant concentration is higher than its CMC, the contaminant is solubilised into the micelle core (See more details in Section 2.8). The oil recovery efficiency of surfactant EOR, especially for biosurfactants, has been reported. For instance, about 90% of the oil was recovered from a refinery oil sludge using rhamnolipid, a biosurfactant produced by *Pseudomonas aeruginosa* (Yan *et al.*, 2012). In a pilot-scale study, the rhamnolipid solution had an oil recovery rate of 98% from a lab-prepared O/W emulsion with waste crude oil in a stirring reactor (150 L). Moreover, the recovered oil has less than 0.3% of water content (Long *et al.*, 2013). However, this emulsion could not represent the complexity of the emulsions found in a real-case scenario, as mentioned before. Some reports evidenced the higher oil recovery efficiency of biosurfactants compared to synthetic surfactants. For instance, a study with a sand contaminated with motor oil showed that the biosurfactants surfactin (*Bacillus subtilis*) and rhamnolipid had an oil recovery rate of 62 (±0.03%) and 57 (±0.58%), respectively. In contrast, the oil recovery rates for the synthetic surfactants, Tween 80, sodium dodecylbenzenesulfonate (SDBS), and Alfoterra 145-5PO were 53% ± (0.01), 51% ± (0.19), and 55% ± 0.48, respectively (Pornsunthorntawee *et al.*, 2008). Also, Lai et al. (2009) reported that rhamnolipids (63%) and surfactin (62%) had a higher TPH removal efficiency from contaminated soil compared to Tween 80 (40%) and Triton X-100 (35%).

According to Hu et al. (2013), surfactant EOR is a cost-effective and fast process because it is not dependent on heating or electromagnetic sources; only a mechanical shaker is needed to ensure the mixing of the surfactants with the oil sludge. Also, the oil recovery efficiency is improved by the selective extraction of the oil with the hydrophobic part of the surfactants. Since this treatment does not need a high specialised equipment as the other oil recovery methods mentioned before, it can be used to treat high volumes of waste on a large scale.

However, issues such as environmental toxicity and recalcitrance by chemical (synthetic) surfactants are significant drawbacks. Therefore, biosurfactants can be considered due to its environmental compatibility and better surfactant activity properties such as lower CMCs (i.e. a low amount of surfactant is needed to have micelles in the solution) compared to chemical surfactants (Pacwa-Płociniczak *et al.*, 2011). Oil sludge washing (OSW) is a type of surfactant EOR treatment. This method is similar to the soil washing process. Section 2.11 discusses in detail the OSW method.

2.6.2. Biological methods

The following methods are based on the use of organisms (e.g. microorganisms and plants) for the biodegradation of PHCs and biotransformation of heavy metals to less toxic forms found in the oil sludge. Therefore, the biological methods aim to reduce the contaminant burden in the sludge, as the incineration, oxidation, and encapsulation methods do.

Landfarming consists in the ***bioremediation*** of the oil sludge by microorganisms in which the oil sludges are added to the upper layer of the in a selected soil area. This mixture is constantly oxygenated with aeration machines with spikes for the proper performance of the added microbiota consortium (Chang *et al.*, 2000; da Silva *et al.*, 2012). This system uses an impermeable layer to avoid leaching, similar to the secure landfilling. Microorganisms are biostimulated with the addition of nutrients such as potassium, nitrogen, and phosphorus (da Silva *et al.*, 2012). The optimum sludge pH and temperature for microbial degradation are from 6 to 8 and from 25 to 35°C, respectively. Temperatures below 15°C or above 40°C should be avoided due to slow degradation rates (Singh *et al.*, 2005). Other physicochemical processes that influence the remediation of oil sludges are volatilization and photo-oxidation processes. For instance, hydrocarbons lower than C_{16} and PAHs with less than three rings could be volatilised under the effect of the sunlight (Singh *et al.*, 2005). Some of the microorganisms reported in the bioremediation of petroleum hydrocarbons are *Acidovorax*, *Pseudomonas*, *Rhodococcus*, *Micrococcus*, *Mycobacterium*, *Alcaligenes*, and *Arthrobacter* (Frick *et al.*, 1999). These last species were reported in the remediation of *n*-alkanes C_{10} to C_{40}. Also, the fungi *Fusarium* and *Penicillium* were used in the bioremediation of these alkanes (Frick *et al.*,

1999). Usually, a bacterial consortium is added in the landfarming system, and each bacterial species can degrade a specific type of compound. This is known as bioaugmentation (Hu *et al.*, 2013). There was about 80% of PHCs removal in an 11 months-landfarming study of oil refinery sludge (Marin *et al.*, 2005). Another study showed a PHCs degradation of almost 90% in the landfarming of oil sludge during two months (Admon *et al.*, 2001). This method is usually selected due to its cost-effectiveness (Harmsen, 1991), low energy requirements and the potential to treat large volumes of oil sludge (Khan *et al.*, 2004). Among the disadvantages, landfarming needs a large surface area for the treatment, and it also requires a longer period compared to other methods (Chang *et al.*, 2000). Moreover, this treatment can produce contamination of groundwater when the area is not properly isolated with the impermeable layer (Japan External Trade Organization (JETRO) *et al.*, 2010). According to Ward et al. (2003) and the Federal Remediation Technologies Roundtable (FRTR, 2015), the use of landfarming for the treatment of petroleum and refinery sludges is banned in most of the federal states in the USA. Another disadvantage is that some contaminant compounds are recalcitrant to microorganisms, so the reduction rates of TPH concentrations cannot be higher than 95% (USEPA, 2004). As rule of thumb, if the TPH levels in the sludge are greater than 50,000 ppm, these concentrations can inhibit the growth of most of the microbiota (USEPA, 2004). In fact, Helmy et al. (2015) recommended decreasing the TPH concentration by washing the sludge with surfactants before the bioremediation process. Another drawback is that the sorption of the contaminant to the matrix (e.g. soil or sludge) can influence the bioremediation process by affecting its bioavailability (Collins, 2007). In general, the costs of the landfarming are between 30 to 60 USD·ton^{-1} of petroleum-contaminated soils, and the time needed can be from to 6 months to 2 years (USEPA, 2016b). As suggested before in this thesis, landfarming could be applied to treat the residuals from the oil recovery method. It is expected that these residuals have minor concentrations that are not harmful to the microorganisms at this point. Moreover, plants can be added in the landfarming area for performing a phytoremediation process to enhance the treatment of the residuals as it is mentioned later in this section. This plants cannot be used for food consumption due to the potential accumulation of residual contaminants in the plant parts. Then, plants with economic benefits such as soybeans can be used for the production of biodiesel.

Phytoremediation of organic chemicals consists of some remediation strategies done by plants which includes rhizoremediation and plant containment (Olson *et al.*, 2003). Rhizoremediation consists on the breakdown of organic pollutants by rhizosphere

microorganisms (Olson *et al.*, 2003). According to Thoma et al. (2003), rhizosphere has the highest rate of degradation of organic chemicals because the plant roots spur the growth of the microorganisms. For example, some studies suggested that the microbial heterotrophic abundance -in the rhizosphere- may be 100-fold greater than that in bulk soil (McCutcheon and Schnoor, 2003). Therefore, the root exudates influence positively in the rhizosphere microorganisms. McCutcheon and Schnoor (2003) reported that these exudates have several biodegradable compounds such as sugars, organic acids, and alcohols, which stimulate the microbial growth with the provision of high levels of carbon and energy (Frick *et al.*, 1999). Olson et al. (2003) mentioned that the benefits of the interaction between plant and microorganisms in a remediation process are the enhancement of pollutant bioavailability, cometabolism, and genetic induction; increase in biosurfactant-producing microorganisms, soil aeration, and microbial biomass; and improvement of soil quality. A disadvantage is that rhizoremediation could take several seasons, so a plant succession is an option for the continuity of the process (Olson *et al.*, 2003). Another method of phytoremediation of petroleum hydrocarbons is the plant containment. This method involves the accumulation of contaminants in the plant lipid content, adsorption on the root surface, and retention within the root zone to avoid contaminant leaching (Frick *et al.*, 1999). McCutcheon and Schnoor (2003) mentioned that phytoremediation and landfarming are more cost-effective, powerful and sustainable in combination than each one alone.

The combination of landfarming and phytoremediation has some advantages. For example, the catabolic process in landfarming usually leads to complete mineralisation into CO_2 and water. Also, microorganisms have the ability to mutate and evolve rapidly (McCutcheon and Schnoor, 2003). On the other hand, plants have the abilities to quickly change some factors such as the pH of soil and water, organic content and nutrient availability (McCutcheon and Schnoor, 2003). Plants produce more biomass than microorganisms, and they have more specific enzymes for the transformation, conjugation, and storage of the contaminant (McCutcheon and Schnoor, 2003). Consequently, the link between plants and microorganisms is positive, and phytoremediation could be enhanced by the combination of plant and microbial enzymes (Wolfe and Hoehamer, 2003). For example, Ramirez and Dussan (2014) reported the use of landfarming with the further phytoremediation of oil sludges. The study found that landfarmed oil sludge provided adequate soil conditions to grow jack beans (*Canavalia ensiformis*) that in turn phytoremediated residual aliphatic and aromatic hydrocarbons in the soil from the landfarmed sludge. In this study, there were no morphological

differences in the leaf area and plant height between the plants growing in the sludge-amended soil and the control plants. Moreover, there was no evidence of phytotoxicity in the plants growing in the sludge-amended soil. Specifically, in this study, rhizo- and phytodegradation reduced the total petroleum hydrocarbons by 57% during the four months of the study (Ramirez and Dussan, 2014).

Biodegradation of oil sludge contaminants using biopiles consists in the mixture of the oil sludges in piles or cells with soil. The system is constantly aerated to enhance microbial activity (da Silva *et al.*, 2012). As in landfarming, this process uses biostimulation (addition of nutrients) and humidification of the contaminated soil matrix. An impermeable layer is used to avoid and prevent the migration of contaminants (e.g. leachates) outside the system (da Silva *et al.*, 2012). In addition, the use of several pierced ducts at the bottom of the biopile optimise the aeration. These ducts are connected to a compressor (Kriipsalu and Nammari, 2010). Some organic materials such as straw, bark, and wood chips can be added as bulking agents. These agents can enhance the air flow and moisture distribution by the increase of porosity (Hu *et al.*, 2013). Since these bulking agents are organic materials, the technique is also known as composting (Marín *et al.*, 2006). The addition of cotton stalk as a bulking agent favoured the TPH removal rate (50%) in the composting process of aged oil sludge for 220 days (Wang *et al.*, 2012). A 373 days-composting pile study showed that the TPH reduction rates from an oil refinery sludge with different bulking agents were 74% (kitchen waste compost), 62% (sand), 51% (matured oil compost), and 49% (shredded waste wood) (Kriipsalu *et al.*, 2007). The use of biopiles is more efficient in the PHCs removal compared to landfarming because the biodegradation can be more favoured by the easy control of the conditions in the biopiles such as aeration and nutrients available in the bulking agents. Also, the volatilisation of the light fractions of organic contaminants can be contained in the auxiliary collection units of the composting treatment vessels (Hu *et al.*, 2013). However, as opposite to landfarming, the capacity of the biopiles is limited to treat only a small amount of oil sludges. Moreover, the duration of the treatment can be longer than landfarming (Khan *et al.*, 2004). In general, the costs of the biopiles are between 30 to 90 $USD \cdot ton^{-1}$ of contaminated soils (USEPA, 2016a). These costs are slightly higher than the landfarming treatment.

Bioreactors and bio-slurry treatment have been used mostly for the treatment of liquid wastes (e.g. oil wastewater sludges). The microorganisms applied for the bioremediation process are usually maintained suspended in a liquid medium that interacts with the soil matrix. Bioreactors have a constant air supply (da Silva *et al.*, 2012). The bioreactor has a rotating

drum to perform an efficient mixing (Woo and Park, 1999). A study of bio-slurry remediation of oily sludge found that the TPH reduction was about 85% after six weeks (Ayotamuno *et al.*, 2007). At large scale, the PHC concentrations in an on-site biodegradation of oil sludge decreased from 20,000 ppm to less than 100 ppm in a 10,000- gallon sequencing batch reactor (SBR) (Maga *et al.*, 2003). Riser-Roberts (1998) and Rizzo et al. (2010) reported that this technique is very useful to treat highly recalcitrant compounds as the constant mixing allows a higher exposure to the contaminants. In fact, the contaminant removal is faster than the landfarming and biopiles treatments (Castaldi, 2003). One disadvantage of this treatment is the high costs associated with the transport of contaminated material and the construction of the system (Alshammari *et al.*, 2008). In addition, the bioremediated products need to be dewatered after the bio-slurry treatment, increasing the costs at this post-treatment stage (Hu *et al.*, 2013).

2.7. General discussion of the current treatments of oil sludges

Before discussing all treatments, it is necessary to make clear that it was no possible to find data related to the costs for most of the treatments of oil sludges specifically except for landfilling (80 – 160 GBP·ton^{-1}), incineration (650 GBP·ton^{-1}) and encapsulation (50 – 150 GBP·ton^{-1}). However, there were some examples of the treatments in other types of matrix such as contaminated soil.

Table 2.2 shows the advantages and disadvantages of the discussed treatments of oil sludge in Section 2.6.

Table 2.2. Advantages and disadvantages of the current treatments of oil sludge.

Main aim	Methods	Advantages	Disadvantages
Direct disposal	Landfilling	- Secure landfilling can ensure that the oil sludge can be completely isolated in one place to avoid any environmental or human health issues	- Leaching and volatilisation of hazardous compounds when no secure landfilling is applied - Large areas are required - The contaminant burden can remain for a long time as no additional treatment methods are applied
Reduction or elimination	Incineration	- Most of the by-products are CO_2 and water - Waste reduced to about 10% of its original volume	- High temperatures needed (750-1200°C) - Clinker formation - Air pollution (secondary pollution) - High operating costs and energy consumption - Costs can increase for oil sludges with high moisture as more volumes of auxiliary fuels are needed
	Oxidation	- PAHs reduction (~ 99%) - Not dependent on temperature and amount of sludge - Highly biodegradable products - Reduced energy consumption - Easy-to-handle reactor. Minimal control and operation required	- It requires a large number of chemical reagents at large scale, increasing the costs
	Encapsulation	- Heavy metals can be immobilised at the stabilisation step - If the solidified treated sludge is used in the production of concrete blocks, a profit can be obtained	- The stability in the solid material (e. g. ceramic blocks) can be compromised due to leaching and weathering of the oil - Chemical alteration of the solid material can compromise its further use due to compounds in the sludge - Limited incorporation of oil sludge into ceramic blocks (10 – 20 wt %), so their stability is not compromised
	Landfarming	- Does not require higher levels of energy compared to the other physicochemical reduction or elimination methods - Bacterial consortium can degrade a variety of specific compounds - Cost effective	- Large areas are required - Long period of treatment compared to the physicochemical methods - If the area is not completely isolated, there are some leachates

Reduction or elimination (cont.)		- Rapid adaptation of microorganisms (gene mutations for contaminant degradation enzymes) - Can treat high amounts of oil sludge	- No degradation of highly recalcitrant compounds (only bioavailable contaminants) - Pretreatment step to reduce the contaminant concentrations to tolerable levels for the microorganisms
	Phytoremediation	- Economic benefits from the plants used (other than for food consumption) - Plants have more specific enzymes for the transformation, conjugation, and storage of the contaminant - Does not require higher levels of energy compared to the other physicochemical reduction or elimination methods - Cost-effective	- Long period of treatment compared to the physicochemical methods. Plant succession is needed to ensure contaminant degradation - No degradation of highly recalcitrant compounds (only bioavailable contaminants) - Pretreatment step to reduce the contaminant concentrations to tolerable levels for the plants
	Biopiles	- The biopile layout with aeration systems can enhance the degradation - More efficient operation than landfarming (enhanced aeration, more nutrient addition to microorganisms with cheaper substrates as bulking agents) - Does not require higher levels of energy compared to the other physicochemical reduction or elimination methods - Bacterial consortium can degrade a variety of specific compounds - Cost-effective - Rapid adaptation of microorganisms (mutation to generate genes for contaminant degradation enzymes)	- Long period of treatment compared to the physicochemical methods - Limited to small amount of oil sludge - No degradation of highly recalcitrant compounds (only bioavailable contaminants) - Pretreatment step to reduce the contaminant concentrations to tolerable levels for the microorganisms
	Bioreactors	- Constant mixing that ensures a high contact of microorganisms with the contaminant - Does not require higher levels of energy compared to the other physicochemical reduction or elimination methods - Bacterial consortium can degrade a variety of specific compounds - Cost-effective - Rapid adaptation of microorganisms (mutation to generate genes for contaminant degradation enzymes)	- Limited to the treatment of liquid oil sludges - High costs at large scale for the construction of the reactor and high energy requirements for the rotating drum system - A post-dewatering step of the bioremediated products - No degradation of highly recalcitrant compounds (only bioavailable contaminants) - Pretreatment step to reduce the contaminant concentrations to tolerable levels for the microorganisms

Oil recovery	Centrifugation	- No chemical addition is needed	- No recovery of heavier oil contents from the sludge - It is necessary to pretreat with demulsifying agents if the oil sludge is highly viscous - High costs at large scale (e.g. high energy required to reach stronger centrifugal forces)
	Pyrolysis	- It is the only treatment that has both aims, the reduction or elimination of the oil sludge and the oil recovery	- High temperatures needed (500-1000°C) - Char formation - Higher levels of energy required when applied at large scale - A pre-dewatering step is required - PAHs as by-products - Higher complexity in the oil recovery process (e.g. strict reaction conditions) compared to other recovery techniques
	Electro-demulsification	- Low energy requirements compared to centrifugation and pyrolysis	- High costs at large scale
	Microwave irradiation	- Higher efficiency in the separation of water compared to the other heating techniques - Faster method compared to other heating techniques - No secondary pollution after irradiation	- Costs can increase at large scale due to the specific type of machinery needed - The recovered oil can have some water remnants left depending on the strength of the W/O emulsion; a post-treatment step is required
	Ultrasonic irradiation	- Violent collisions improves the breaking W/O emulsion in the sludge - No secondary pollution after irradiation - Faster method compared to other heating techniques	- High costs at large scale (high levels of energy and expensive machinery)
	Freeze/thaw	- Dewatering removal ratios are high (≥ 90%).	- Freezing can take a long time (except in cold regions), and it can require high intensive energy
	Solvent extraction	- “Like dissolves like”: Organic solvents can extract the oil - Can treat high amounts of oil sludge - Possibility of recycling the oil with the distillation of the recovered oil and solvent mixture	- Heating needed in solvent recycling - High volumes of solvent needed at large scale; increasing costs - Emissions of solvent vapours have potentially hazardous effects on human health and the environment if the system is not completely closed.

Oil recovery (cont.)	Froth flotation	- A simple method to perform. No complex operations or reactions involved - Less expensive compared to other methods as does not need high amounts of energy	- Limited to oil sludges with low viscosity - Recovered oil can have remnants of moisture - A pretreatment is necessary to reduce the viscosity and the coarse sediment particles in the oil sludge - Non-effective treatment in the desorption of oil from the sediments in the oil sludge
	Surfactant EOR	- Can treat high amounts of oil sludge - Amphiphilic nature of surfactants allows the access to both the hydrophilic and hydrophobic parts of the sludge - It is not dependent on heating or electromagnetic sources	- Environmental toxicity of the synthetic surfactants - High costs for production of biosurfactants

Table 2.2 shows the methods grouped according to their aims. To date, these three aims in the treatment of oil sludges are the direct disposal, reduction or elimination, and oil recovery. The first method discussed is the landfilling, and this is the only direct disposal treatment. This treatment can be considered only as the last option of the management of oil sludge if no other methods are available. However, there is a need to guarantee that the landfilling is done securely by the impermeabilisation of the landfill area to avoid any leaching. Also, landfilling can be criticised as a method that only holds the sludge without any treatment of the contaminant.

Among the reduction or elimination methods, the encapsulation (solidification/stabilisation) is different compared to the other reduction treatments because it is the only one that can have a profit by the fabrication of ceramic or cement construction blocks. In addition, heavy metals are immobilised at the stabilisation step. This immobilisation is important because the heavy metals cannot be degraded. However, there are some concerns related to other compounds in the oil sludge (e.g. chemical oil additives) that can compromise the integrity of the ceramic or cement block. Also, leaching and volatilisation of the contaminants from the sludge can be a problem if the weight percent is higher than 20%. Moreover, the commercialisation of this type of ceramic blocks is difficult because some people will be sceptical of using these blocks knowing its composition. Indeed, it is needed more studies to have solid evidence that these type of blocks can be used safely without affecting the integrity of the block.

The oxidation treatment has more advantages compared to the other physicochemical methods in which the main goal is to reduce or eliminate the contaminants. For example, this treatment is not dependent on the temperature, so the oxidation reaction does not require high amounts of energy. Also, this method is not dependent on the amount of oil sludge, and the control and operation are not complex. Moreover, this treatment can enhance the biodegradation of PAHs. The disadvantages of the application at large scale are that the costs increase due to a higher volume of chemical reagents required, and that the oxidation treatment does not have the possibility to recover the oil. However, it is recommended to perform a costs analysis to see if it is worth the investment in the chemical reagents compared to the efficiency of this method at a large scale.

If the chosen reduction or elimination method (e.g. incineration or oxidation) succeeds in the complete elimination of the contaminants, this treatment can be used. Moreover, if the

method is very efficient in terms of energy investment, machinery and costs, undoubtedly this method should be employed. In fact, this will eliminate the need to treat any residuals further as in the oil recovery methods. However, these methods generate secondary pollutants such as VOCs and currently, the application of these reduction or elimination methods at a large scale is limited.

The biological methods also have several advantages as the oxidation treatment has. In fact, these methods are cost-effective, and it does not require high amounts of energy. However, these methods are limited to oil sludges that have contaminant concentrations tolerable to the microorganisms or plants used. Therefore, it is required to pretreat the oil sludge. These methods require more time to achieve a significant reduction of the contaminants. Also, it is necessary to have some regular checks for aeration, biostimulation (i.e. addition of nutrients) and bioaugmentation (i.e. addition of microorganisms) of the bioremedial microorganisms. However, the bioremediation techniques can be applied to treat the residuals from another treatment as mentioned before. Among the biological treatments available, landfarming and phytoremediation are preferred over the use of biopiles and bioreactors because the latter methods are limited to the amount of oil sludge and are more expensive due to the requirement of reactors and other apparatus. In conclusion, the best approach is to use landfarming and phytoremediation combined as both methods are more powerful than alone. Also, these methods are not restricted to the amount of oil sludge treated compared to the limitations found in the biopiles and bioreactors. Moreover, a profit can be obtained by using plants with an economic benefit (e. g. production of biodiesel with soybeans).

The advantage of the oil recovery methods is that the possible reuse of the recovered oil as a feedstock for fuel production. Therefore, a profit can be obtained from the reuse of the oil. Among the oil recovery methods that use energy to recover the oil, microwave irradiation is the treatment with the highest oil recovery efficiency, and it is the fastest method. In addition, the microwave irradiation has the advantage that does not have any secondary pollution. However, this approach can be expensive on a large scale compared to other oil recovery methods such as surfactant EOR or froth flotation.

Pyrolysis is unique among the oil recovery strategies for two reasons. First, this method can reduce the original volume of the oil sludge by burning as the incineration method does. Second, it can recover the oil by transforming the VPHs products into a liquid state which can

be reused as feedstock for fuel production. However, the pyrolysis treatment needs more rigorous operations for the reaction (e.g. setting inert conditions with N_2).

The solvent extraction scheme proposed by AERCO (1995) (Figure 2.5) can be an appropriate example of the adaptation of any treatment of oil sludges for a large scale scenario because this scheme is based on a closed system. In fact, this idea of a closed system is beneficial in terms of the potential hazardous exposure to human health and the environment. Also, this scheme proposed a cyclic process in which the reagents used in the treatment are reused. The large scale scenario suggested by Yang et al. (2005) (mentioned before in the electro-demulsification part from section 2.6.1) can be ideal for the application of an oil sludge treatment at large scale. These authors mentioned that the oil sludge storage tanks could be used directly as the cells to perform the electro-demulsification process. By doing this, it is not necessary to invest in transportation and adaptation of other locations for the treatment of oil sludges. Indeed, this idea can be applied to other treatments such as the surfactant oil recovery. In this case, the whole oil sludge storage area can be adapted as well as the treatment area.

In general, it can be concluded that the weakest treatment is centrifugation among all of the methods. First, this method needs to have a pretreatment of high viscous oil sludge. Also, it needs a post-treatment of the sediment as some heavy fuel components can still be attached. Second, the costs are high at large scale due to the adaptation of a bigger centrifuge and the use of high levels energy needed to reach the high centrifugal forces. Even though this method itself does not require any chemical addition, sometimes the oil sludge can have a high viscosity. Therefore, it is necessary to add demulsifiers or solvents to achieve a successful oil recovery.

In summary, it can be inferred from the current treatments available that various combinations of different methods can lead to an appropriate management of the oil sludges. The use of one combination will depend on the availability of materials and locations. For instance, the surfactant EOR method can be applied as a pretreatment of the sludges to break the W/O emulsion to recover the oil. Then, the combination of landfarming and phytoremediation can treat the residual sludge, if necessary, as mentioned before. Other examples include the use of the oxidation treatment combined with bioremediation techniques such as landfarming and the combination of surfactant EOR with microwave irradiation. The latter approach involves the enhancement of the emulsion breaking by the surfactants and the

recovery of the oil by the microwave irradiation with no secondary pollution, as mentioned before. In fact, this method is ideal, but the application to a large scale is challenging.

As mentioned in Section 2.1, the main objectives of the treatment of oil sludges are currently based on their reduction, re-utilisation, and recycling (the 3R concept) (Sakai *et al.*, 2011). Also, the European Community addressed the importance of the prevention, recovery, and reuse of waste oils (European Parliament, 2008). Therefore, the oil recovery techniques seem to be an appropriate choice. These methods have different strategies to achieve the oil recovery. Centrifugation, pyrolysis, electro-demulsification, microwave and ultrasonic irradiation use energy sources to break the W/O emulsion in the oil sludge. In the case of freeze/thaw, solvent extraction, froth flotation, and surfactant EOR, these methods are based on other physicochemical to achieve the demulsification. For example, solvent extraction relies on the solubility of the solvents in the oil sludge. However, the methods which depend on high amounts of energy and specific machineries such as pyrolysis and ultrasonic irradiation can be considered to be more expensive to use at a large scale.

Having in mind that the best approach for the treatment of oil sludges is the use of an oil recovery method instead of a disposal treatment, surfactant EOR and microwave irradiation are both efficient and less expensive compared to other methods (Hu *et al.*, 2013). Also, these methods allow the possible reuse of the recovered oil as a feedstock for fuel production (Giles, 2010) and the reduction of the contaminant burden in the sludge. However, microwave irradiation requires more specialised and costly equipment, so the application at a large scale is more limited. For these reasons, surfactant EOR seems to be an appropriate technique to use because it is a fast and efficient process. In addition, it can be used for the treatment of high amount of oil sludge, and the surfactants have the ability to take the oil in the hydrophobic core of their micelles as mentioned previously (Hu *et al.*, 2013). However, these authors mentioned that some limitations include toxicity of some surfactants and the costs involved in the biosurfactant production that can be high. Also, as it was noted before, the surfactants are widely used in different oil recovery treatments to enhance the demulsification and consequent recovery of oil from the sludge. Specifically, it has been reported that surfactants were used to improve centrifugation, electro-demulsification, microwave irradiation, and froth flotation. Therefore, this information can imply the usefulness of surfactants in the oil recovery.

In conclusion, surfactant EOR was selected and analysed in this thesis due to the advantages mentioned before and its potential application at a large scale. Consequently, the

next sections include a discussion about the generalities of surfactants and their application in the oil recovery from oil sludges.

2.8. Surfactants

The word *"surfactants"* stands for an abbreviation of surface active agents, which have the main function of lowering the surface and interfacial tensions of liquids. Surface or interfacial tension is the force per unit of length applied to the perimeter of a surface (Schramm, 2000b). If the surface separates a gas (air) and a liquid (water), it is called surface tension. When the surface separates two nongaseous phases (oil and water), it is known as interfacial tension (Schramm, 2000b). Adsorption of the surfactant at the interface between the oil and water solutions is similar to the water and air interface. However, the effectiveness of interfacial reduction by a surfactant is greater in the aqueous-oil interface compared to the water-air interface (Rosen and Kunjappu, 2012). Surfactants are characterised by their amphiphilic properties due to the presence of both hydrophilic and hydrophobic groups (Barnes and Gentle, 2005). Figure 2.6 shows the amphiphilic structure of surfactant monomer in which a hydrophilic (polar) head joins to a hydrophobic or lipophilic (non-polar lipid) tail (Christofi and Ivshina, 2002). Moreover, the amphiphilic properties confer the ability of partition at the different interface of phases (e.g. air/water, oil/water) and several states of hydrogen bonding and polarity in the case of O/W emulsions.

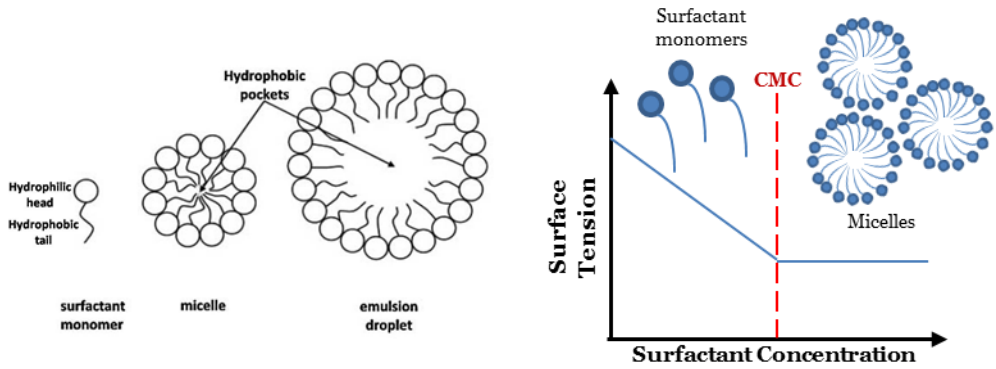

Figure 2.6. Structure of surfactants and formation of micelles (left); adapted from Elliot et al. (2011). Relationship between surface tension and surfactant concentration, CMC (critical micelle concentration) (right); based on Pacwa-Płociniczak et al. (2011).

The balance between the hydrophobic and hydrophilic portions of the monomers provides the surfactants with their key properties such as the formation of micelles and accumulation and adsorption at different interfaces (Tadros, 2005a). Surfactant monomers can be joined to form a micelle. Micelles are colloidal-sized clusters with spheroid or lamellar structures. These have their hydrophobic tails toward the centre of the micelle forming the hydrophobic pocket that allows partition of the hydrophobic contaminant (solute); the hydrophilic heads are found towards the solvent (Figure 2.6) (Rosen and Kunjappu, 2012). These clusters give to the surfactants their solubilisation properties. Micelles can adopt different shapes such as spherical, globular, and cylindrical (Champion *et al.*, 1995). These morphology changes depend on the pH, temperature, ionic strength of the solvent, and the concentration of the surfactant (Champion *et al.*, 1995). Also, when hydrocarbons are solubilised inside the hydrophobic micelle core, the size of the micelle can increase. This increase can lead to a deformation of the micelle by losing its symmetry of spherical shape and turning it into a lamellar shape (Rosen and Kunjappu, 2012).

The micelles formed at the critical micelle concentration in which the surfactant monomers are grouped into the round shape micelles (Figure 2.6). The CMC is essential to study the performance of a surfactant, and it is the concentration of surfactant at which the micelle formation is favoured by the thermodynamics of the surfactant-solvent matrix (Haigh, 1996). Before the CMC, the solution has the surfactant in a monomeric state. When the surface tension has decreased abruptly in a polar solution, the CMC is reached. Then, the surface tension stops dropping and stabilises at concentrations higher than the CMC (Schramm and Marangoni, 2000).

When both surface tension and concentration of the surfactant are plotted, the tendency is that the surface tension decreases smoothly to a lower limit, and then it remains constant at this lower level as shown in Figure 2.6 (Barnes and Gentle, 2005). For example, the reduction of surface tension achieved in water by surfactants ranges from 72 $nM \cdot m^{-1}$ to 27 $nM \cdot m^{-1}$ (Christofi and Ivshina, 2002). By testing the surface tension reduction in water, the surface effectiveness of a surfactant can be assessed. Therefore, the surface tension reduction is related directly to the surfactant effectiveness (Schramm, 2000a). Surfactants are involved in the promotion of emulsification, solubilisation, and wetting of several types of inorganic and organic compounds (Elliot *et al.*, 2011). For instance, if the concentration of surfactant exceeds the CMC, the ability of solubilisation of hydrophobic compounds increases significantly due to the presence of the micelles (Haigh, 1996). Micelles sequester these compounds in the core

of the micelle as mentioned before. Physical characteristics of the hydrophilic polar head such as size and type of structure can influence the CMC value of the surfactant. For instance, when the heads are large and non-ionic, micelles are formed at lower concentrations than the concentrations needed by small ionic heads (Held, 2013). Since the CMC value is a key parameter, it is important to understand the factors that contribute to this value in aqueous media in more detail.

According to Rosen and Kunjappu (2012), the variation within the hydrophilic and hydrophobic groups in a surfactant can considerably affect the CMC value. In the case of the hydrophobic group, the CMC value decreases by increasing the number of carbon atoms in this group. For instance, a reduction in the CMC to about one-tenth of a non-ionic surfactant CMC original value is achieved by increasing twice the methylene units in the hydrophobic group of the surfactant (Rosen and Kunjappu, 2012). Surfactants with either large hydrophobic or hydrophilic groups have high CMC values. For example, an addition of a polar group (*e.g.* -O-, -OH) into the hydrophobic part can generate a substantial increase in the CMC value of the surfactant (Rosen and Kunjappu, 2012). Regarding the hydrophilic group, the CMC will increase if the surfactant has more than one hydrophilic groups (Rosen and Kunjappu, 2012).

Surfactants can be divided based on the ionic charge. The charge is based on their hydrophilic head which influences their ionic nature (Rosen and Kunjappu, 2012). These surfactants can be anionic or charged negatively (e.g. sodium dodecyl sulphate, SDS; sodium hexadecanoate or palmitate), cationic which are charged positively (e.g. hexadecyl(cetyl)trimethyl ammonium bromide, CTAB; dodecyl pyridinium bromide), and zwitterionic or amphoteric with presence of both anionic and cationic states (imidazoline carboxylates and sulfobetaines) (Rosen and Kunjappu, 2012). Anionic surfactants are used widely in the industry (e.g. they are added in most types of detergents) because of their low production costs (Tadros, 2005a). Their detergent efficiency is found in their hydrophobic part which is a linear alkyl group; linear chains are preferred instead of branched chains due to the high effectiveness and degradability of the former (Tadros, 2005a). The hydrophilic groups can be carboxylates, phosphates, sulphonates, and sulphates.

Non-ionic surfactants have an uncharged hydrophilic head group, and therefore, they can be more compatible when mixed with different types of surfactants (Rosen and Kunjappu, 2012). The hydrophilic part of these surfactants is commonly based on their ethylene oxide parts (Tadros, 2005a). These surfactants have the ability to break hydrophobic interactions and

have a low CMC. An advantage of using non-ionic surfactants is that they produce low quantities of foam (Schramm, 2000a). Also, non-ionic surfactants can be petroleum demulsifiers (Rosen and Kunjappu, 2012). A negative characteristic of these surfactants is that their solubility in water diminishes as the temperature increases; the hydrogen bonds break at this point (Hinze and Pramauro, 1993). Then, when the cloud point is reached at a particular temperature depending on the surfactant, the surfactant molecules separate from the solution generating a cloudy appearance due to the surfactant-rich phase. Indeed, it is relevant to know the cloud point, especially when the temperature is an important variable (Nasr-El-Din, 2000). Non-ionic surfactants are divided into different classes depending on the structure of both their hydrophilic and hydrophobic parts: alkyl phenol and fatty ethoxylates, ethoxylates fats and oils, amine ethoxylates, fluorocarbon and silicone surfactants, surfactants derived from mono and polysaccharides, alcohol ethoxylates, and derived ethoxylated sorbitan esters (Tadros, 2005a).

Tween detergents are non-ionic ethoxylated esters composed of polyoxyethylene sorbitan esters of fatty acids. These surfactants are water soluble and have a high hydrophile-lipophile balance (HLB) compared to other non-ionic surfactants (Tadros, 2005a). The HLB is a value from an empirical scale from oil-soluble to water-soluble surfactants (Schramm, 2000b). HLB scale considers values from 0 to 20 for non-ionic surfactants where values less than 9 corresponds to lipophilic surfactants and values greater than 11 refers to hydrophilic surfactants. As a reference, most of the ionic surfactants have HLB values greater than 20 (Schramm and Marangoni, 2000). Tween 80 (T80) belongs to the group of long-chain carboxylic acid esters, and it produces low quantities of foam compared to other non-ionic surfactants such as the Triton X series (Rosen and Kunjappu, 2012).

The reaction between octylphenol with ethylene oxide creates the Triton X series surfactants [tert-octylphenol poly (ethyleneglycolether)n]. These surfactants are considered to be octyl phenol ethoxylates (Tadros, 2013). These chemical surfactants are emulsifiers and oil wetting agents and they are included in the group of alkyl aryl polyether alcohols (Arnold and Linke, 2007). The ether side chain of these surfactants contains a particular average number of ethylene oxide (EO) units which are used in their nomenclature. Triton X-100 (TX100) has 9 to 10, and Triton X-114 (TX114) has 7 to 8 of EO units in average (Arnold and Linke, 2007). These EO units are necessary because they can enhance the hydrophobic nature of the surfactant and the adsorption onto polar surfaces. Also, the EO units can increase the solubility of the surfactant in organic solvents (Rosen and Kunjappu, 2012). These characteristics can be relevant for the performance of the surfactant in the oil sludge washing process. For instance,

non-ionic surfactants with EO units are excellent dispersants for carbon related molecules (Rosen and Kunjappu, 2012). Also, as the amount of EO units in a surfactant increases, the CMC reduces (Al-Sabagh and Atta, 1999).

2.9. Use of biosurfactants as an alternative to synthetic surfactants

Biosurfactants are a type of surfactants produced by microorganisms and plants. The hydrophilic moiety of these biosurfactants is composed by mono-, di- or polysaccharides, and amino acids. On the other hand, the hydrophobic moiety consists of saturated, unsaturated, hydroxylated fatty acids or hydrophobic peptides (Banat, 1995; Rosen and Kunjappu, 2012). In fact, their benign environmental status is due to their composition of glucose (hydrophilic part) and fatty alcohols (hydrophobic part) (Tadros, 2005a). An advantage of biosurfactants compared to synthetic surfactants is that these biological surfactants can be produced from renewable sources such as glucose, glycerol, olive oil, ammonium salts, urea, and *n*-alkanes (Nguyen *et al.*, 2008). In fact, these could save some costs as the production of biosurfactant is expensive. For instance, the purchase of only 10 mg of rhamnolipid can be over £300 (AGAE Technologies). Moreover, biosurfactants have been used in microbial enhanced oil recovery (MEOR) and oil spill control because these compounds are biodegradable and non-toxic and can be as effective as the synthetic surfactants (Banat, 1995; Rosen and Kunjappu, 2012).

Some biosurfactant-producing microorganisms are: *Pseudomonas aeruginosa* (rhamnolipid, RL), *Arthrobacter* MIS38 and *Bacillus licheniformis* JF-2 and 86 (lipopeptide), *Candida antarctica* (mannosylerthritol lipid), *Corynebacterium insidiosum* (phospholipid), *Pseudomonas fluorescens* (lipopeptides), *Rhodococcus* sp. ST-5 and H13-A (glycolipid) (Banat, 1995), *Bacillus mohjavens* and *B. licheniformis* (lichenysin), *Acinetobacter venetianus* (emulsan), *Pseudomonas aeruginosa* (rhamnolipid), and *Bacillus subtilis* (surfactin) (Zheng *et al.*, 2012). The latter two are the most used surfactants for oil recovery studies due to their higher efficiencies (Pornsunthorntawee *et al.*, 2008; Joseph and Joseph, 2009; Lai *et al.*, 2009; Yan *et al.*, 2012; Zheng *et al.*, 2012). Since the biosurfactant production costs are elevated, it has been proposed to enhance the biosurfactant yields by using waste substrates (Hu *et al.*, 2013). Alternative sources include palm, olive, grapeseed, and sunflower oil, molasses, olive oil, potato processing effluents, and glucose (Pornsunthorntawee *et al.*, 2008).

Biosurfactants are divided into low-molecular-mass and high-molecular-mass biosurfactants. Compounds with low-molecular-mass include glycolipids (rhamnolipids, trehalolipids produced by *Arthrobacter* sp. and *Corynebacterium* sp., and sophorolipids by *Torulopsis* spp.), phospholipids (phosphatidylethanolamine by *Acinetobacter* sp. and *Rhodococcus erythropolis*), and lipopeptides (surfactin and lichenysin). This type of biosurfactants is involved in the decreasing of both surface and interfacial tensions, and also are demulsifiers (Pacwa-Płociniczak *et al.*, 2011). In contrast, high-molecular-mass biosurfactants are more efficient at stabilising oil-in-water emulsions (emulsification). These compounds include bioemulsifiers such as lipopolysaccharides (emulsan) and lipoproteins (Pacwa-Płociniczak *et al.*, 2011). Plants also are potential biosurfactant-producing organisms. The most common plant biosurfactants are guar, aescin, tannin, lecithin, guar gum, and saponin. To sum up, biosurfactants are preferred because of their high surface activity, low toxicity, high degradability, high foaming activity and stability due to its lower CMC, and high stability at extreme salinities, pH, and temperatures (Torres *et al.*, 2011; Chandankere *et al.*, 2013).

Biosurfactants have been used in the enhancement of petroleum hydrocarbons degradation in oil spills due to their solubilisation abilities (Banat, 1995). To illustrate, rhamnolipids are used for the separation of emulsions which are generated in the oil sludge (Huang *et al.*, 2013). In addition, Sarkar et al. (1989) reported the increasing interest of researchers on the use of biosurfactants in soil bioremediation because they can contribute to hydrocarbon degradation (Banat, 1995) due to their enhanced interfacial properties (Rosen and Kunjappu, 2012). For example, Whang et al. (2008) reported from in an 88 days-study that the TPH degradation with RL from a diesel contaminated soil was 97% with the addition of rhamnolipid whereas with the control was 47%. Another use of biosurfactants is in the bioavailability of organic and inorganic contaminants (Champion *et al.*, 1995). As biosurfactants increase the bioavailability of organic compounds, these compounds also can join in complexes with metals to enhance metal bioavailability (Pacwa-Płociniczak *et al.*, 2011). This feature of the biosurfactants is important to consider since oil sludge also contains heavy metals as mentioned before.

2.10. Soil washing

Soil washing is used to remediate inorganic (metals) and organic (oil hydrocarbons) contaminants from soils (Semer and Reddy, 1996). This *ex-situ* process consists of a high contact between the soil matrix and the aqueous solution (Semer and Reddy, 1996; Lau *et al.*, 2014). According to Semer and Reddy (1996), first, the contaminated soil is excavated and extracted. Then, the washing process is applied, and a solid/liquid separation occurs. After that, a wastewater treatment protocol is used to treat residues (leachates) from the washing. Finally, the soil is returned to its original location (Semer and Reddy, 1996). Urum and Pekdemir (2004) applied the use of biosurfactants in soil washing processes. In fact, the soil washing efficiency has been higher for biosurfactants compared to synthetic surfactants. For instance, Lai et al. (2009) showed that the higher TPH removal efficiency in a soil washing process was achieved by rhamnolipid (63%) and surfactin (62%) compared to synthetic surfactants, Triton X-100 (40%) and Tween 80 (35%).

2.11. Oil sludge washing (OSW)

Due to the potential application of washing in the decontamination of soils, some studies have been applying this technique to the treatment of oil sludges. Zheng et al. (2012) developed a washing process to recover oil from oil sludge using biosurfactants based on the soil washing methods employed by Urum et al. (2003), Urum et al. (2004), Urum and Pekdemir (2004). Briefly, the oil sludge washing (OSW) at lab-scale consists in adding a certain quantity of surfactant to the oil sludge with a co-solvent to enhance the process. Then, the matrix is mixed by mechanical shaking. In the end, the mixture is left to settle for allowing separation into three phases (pure oil, oil-water emulsion, and solids and sediments). Then, the recovered oil is the pure oil and the oil layer from the emulsion. Finally, the recovered oil can be mixed with crude oil to improve its quality (Abdel Azim *et al.*, 2011). Both the reduction of the interfacial tension of the W/O emulsion in the sludge by the surfactants and the agitation performed in the washing leads to the breaking of the emulsion (Rosen and Kunjappu, 2012). Figure 2.7 shows the mechanism by which the surfactants demulsify the W/O emulsion of the oil sludge. Briefly, the surfactant reduces the hydrophobic nature of the water and oil interface of the emulsion. Consequently, the viscosity reduces, and the surfactant is incorporated into the interface. The

hydrophilic heads are directed towards the water and the tail of the surfactant monomer is in the oil phase. Finally, the emulsion is broken by the displacement of the emulsifying agents to the oil phase.

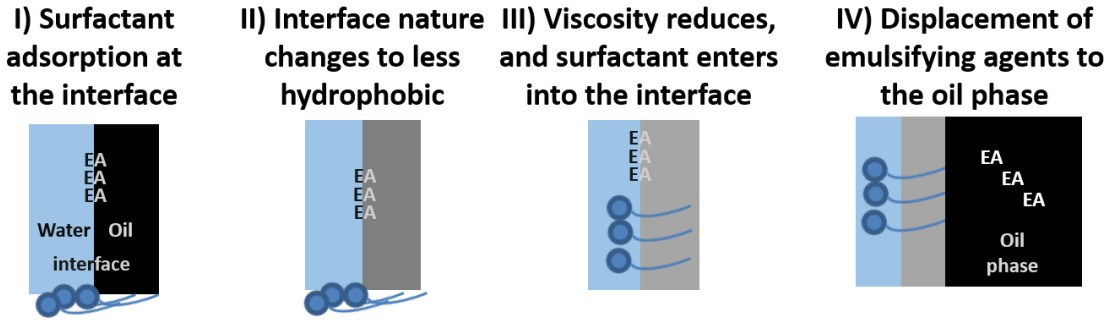

Figure 2.7. Demulsification mechanism of a W/O emulsion based on Rosen and Kunjappu (2012). EA: Emulsifying agents (e.g. asphaltenes, resins and waxes from the crude oil). Each surfactant monomer is depicted with its hydrophilic head and hydrophobic tail. The blue and black portions represent the water and the oil, respectively. The grey colour gradient from II) to a light grey colour in IV) is intentional to show the viscosity reduction in the interface film. At the end of demulsification (IV), it is observed a region (light grey colour) which belongs to some remnant oil in the surfactant solution.

To date, there are no studies that test the performance of different surfactants in the washing of oil sludges and their effect of their concentration and application ratios to the sludge, specially in different types of oil sludges. However, there are several investigations about some parameters of the OSW such as the surfactant to soil matrix or sludge ratio, washing time, shaking speed, and temperature in other matrices such as soils and oil-based drill cuttings. For instance, Yan et al. (2011) in their work of biosurfactant washing of oil-based drill cuttings have found that when the surfactant solution to oil drill cutting ratio is increased from 1:1 to 3:1, it can be removed about 80% of total extractable organics (TEO). However, the increase in the recovery was reduced at higher ratios (i.e. 4:1, 5:1). In the case of T80 and TX100, Peng et al. (2011) showed that these surfactants had a greater capacity of solubilisation because there was a 90% oil removal from soil when more surfactant solution was added (20:1) compared to a 0% removal in a 1:1 ratio. Yan et al. (2011) found a quick elimination in the first 10 minutes with more than 67% of TEOs displaced from oil-based drill cuttings; the removal process then

stabilised until 50 minutes. Also, Peng et al. (2011) showed a quick oil removal using T80 and TX100 from 30 to 60 min that tends to stabilise at the latter time.

Regarding the shaking speed, Yan et al. (2011) reported that the removal of oil was the same from 200 to 350 rpm. Moreover, Peng et al. (2011) found that the optimal stirring speed for PAH removal was 250 rpm, and then the removal decreases at 300 rpm. Shaking or stirring, as a mechanical process, is related to the collision between sludge particles that lead to the decoupling of sediment particles (Peng *et al.,* 2011). These authors also demonstrated that an extraction period of 60 minutes was optimal to achieve oil removal; beyond 60 minutes the removal percentage remained stable.

Rising temperatures can reduce the oil viscosity, so TEO removal was enhanced when the temperature increased from 20 to 60°C. However, TEO removal did not improve at temperatures higher than 60°C (Yan *et al.,* 2011). Schramm and Marangoni (2000) stated that CMC values do not depend strongly on the pressure and temperature, but the values are highly affected at temperatures greater than 100°C. Rosen and Kunjappu (2012) mentioned that there is a minimal effect of temperature on a rhamnolipid solution, whereas non-ionic surfactants are affected due to their cloud points, as noted before.

Co-solvents are non-surface active compounds that enhance the effectiveness of the surfactant (Schramm, 2000b). These can be either non-polar (hydrocarbons solvents such as cyclohexane and pentane) or polar nature (alcohols such as *n*-butanol and isopropanol). Also, the properties of the interfacial film are modified, and this leads to a coalescence and separation of the emulsion (Sjöblom *et al.*, 1990). In general, the addition of organic co-solvents can aid in the dissolution of the surfactant used (Sjöblom *et al.,* 1990), so these co-solvents can be utilised in the OSW process. For instance, toluene was used as the co-solvent to aid in the oil recovery by the surfactants on the pilot study of Chapter 4 of this thesis. This solvent has been used before by El Naggar et al. (2010) and Atta and Elsaeed (2011) to extract oil. At this point, it is important to mention that a co-solvent is not the same as a co-surfactant. A co-surfactant is a surfactant that is added to enhance the primary surfactant efficiency in a surfactant mixture (Schramm, 2000a), and the co-solvent is the polar or non-polar solvent added in the OSW.

Co-solvents such as alcohols have been used in the petroleum industry to optimise the performance of surfactants in EOR, and their advantage is that most of them can be miscible either in polar solutions or with a small degree of non-polarity (Lowe *et al.*, 1999). The use of alcohol as co-solvent aids the surfactant film to be less rigid. This condition leads to the

prevention of unwanted viscous phases and emulsion formation (Hirasaki *et al.*, 2011). Lowe et al. (1999) mentioned that the use of low-molecular-weight alcohols can be advantageous for upward mobilisation of non-aqueous phase liquids (NAPLs) because these are less dense than water. Also, Sjöblom et al. (1990) reported that the use of 1-butanol, benzyl alcohol or other medium-chain alcohols and amines could enhance the separation of water. In addition, these authors mentioned that 1-butanol and 1-pentanol (medium-chain alcohols) could be de-emulsifiers in the system by breaking almost the entire emulsion after 24 hours. However, they reported that more complex alcohols (e.g. branched) such as isopropanol did not improve the destabilisation of the emulsion (Sjöblom *et al.*, 1990). It has been reported that polar co-solvents such as alcohols are appropriate to use in the recovery of oil with a high degree of aromaticity (Khodadoust *et al.*, 2000). However, when the oil hydrocarbons are highly saturated, a non-polar co-solvent is considered.

The reason for selecting organic hydrocarbons as co-solvents instead of alcohols is because the former have a better performance in the solubilisation of complex hydrophobic contaminants (Jafvert, 1996) such as the pollutants found in the oil sludges. This solubilisation is based on the rationale that "like dissolves like" (Hansen, 2007), which is a characteristic to be noted in the selection of solvents (Li *et al.*, 2012). In this case, these solvents are in the range of the solubility of the oil pollutants found in the oil sludges. For instance, Abouelnasr and Zubaidy (2008) found that iso-butanol and isopropanol only had about 8% of recovered oil compared to heptane (25%), hexane (18%), LPG condensate (30%), and methyl ethyl ketone, MEK (35%) from the oil sludge. Sometimes, another disadvantage of using alcohols as co-solvents in highly hydrophobic matrices is that these solvents can increase the interfacial tension achieved by the surfactant in the system due to a decrease in the solubilisation of oil and water (Salter, 1977). For all these reasons, non-polar co-solvents were used in this thesis.

After the OSW, a freezing/thawing treatment can be applied. This treatment can aid in the recovery of the unfrozen oil top layer with the co-solvent and the performance of dewatering by the coalescence of water droplets from the W/O emulsion formed (Hu *et al.*, 2015). Figure 2.8 depicts the freeze/thaw treatment. First, the freezing step reduces the thickness of the interfacial film (water/oil) gradually until the film breaks by the formation of water ice crystals below the water melting point. At this stage, the adjacent water droplets connect each other by the ice crystals. Then, the coalescence of the water droplets occurs during the thawing process with a further gravitational settling of the water droplets in the bottom layer with sediments from the sludge. The oil is recovered on the top (Hu *et al.*, 2013; Hu *et al.*, 2015).

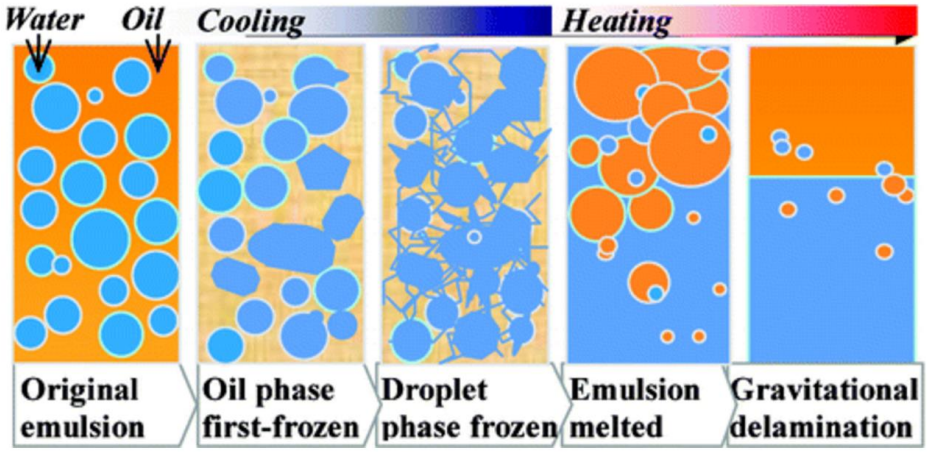

Figure 2.8. Freeze/thaw treatment in an oil/water emulsion after Lin et al. (2008).

It was reported that one cycle of freeze/thaw treatment can be sufficient for achieving dewatering as there were not significant differences among three cycles ($p > 0.05$) with cyclohexane, methyl ethyl ketone, or dichloromethane were used (Hu *et al.*, 2015). In addition, surfactants play a role during the freezing and thawing (Chen and He, 2003). First, surfactant molecules are diffused into the oil phase from the ice lattices at the oil-water interface, and also more surfactant molecules can be separated from the interface during the thawing process. Finally, the surfactant micelles with the recovered oil are found in the thawing step (Chen and He, 2003). When surfactants are not present in the system, the formation of larger water droplets can enhance the coalescence due to a rapid gravitational settling. The slower the thawing process, the better the formation of larger water droplets (Chen and He, 2003; Hu *et al.*, 2015).

The oily phase from the sludge slightly changes the CMC because the surfactant does not dissolve in this phase and it solubilises the oil hydrocarbons into the micelle core (Rosen and Kunjappu, 2012). Specifically, Rosen and Kunjappu (2012) explained that this is the case for saturated aliphatic hydrocarbons. However, unsaturated short-chain hydrocarbons or aromatic hydrocarbons can decrease the CMC, particularly for the more polar hydrocarbons. These hydrocarbons can be adsorbed on the surface of the micelle (hydrophilic heads from surfactant), and then decrease the CMC facilitating the micellisation (Rosen and Kunjappu, 2012).

Recently, biosurfactants have been used in oil recovery studies from oil sludge (Joseph and Joseph, 2009; Yan *et al.*, 2012; Zheng *et al.*, 2012; Long *et al.*, 2013). Especially, rhamnolipids produced by *Pseudomonas aeruginosa* SP4 and surfactin from *Bacillus subtilis* PT2 are commonly used in oil recovery (Pornsunthorntawee *et al.*, 2008). For instance, Zheng et al. (2012) demonstrated that rhamnolipids had more significance (F calculated ratio = 157.61; the next important factor was pH with an F calculated ratio = 140.14) in a study that considered pH, biosurfactant concentration, salinity, and *n*-butanol as a co-solvent. According with the results found by these authors, the optimum oil recovery (74%) in this sludge washing process was achieved through the combination of the following factors: 2 $g \cdot L^{-1}$ of rhamnolipid, 10 $g \cdot L^{-1}$ of NaCl, and 5 $g \cdot L^{-1}$ of *n*-butanol as a co-solvent at pH 12.0, 200 rpm of shaking speed, and 20°C for one hour (Zheng *et al.*, 2012).

Yan et al. (2012) evaluated the temperature, inoculum concentration (%), C/N ratio, and sludge/water ratio (v/v). The rhamnolipid-producing microorganism used was *P. aeruginosa* F-2. The oil sludge used in this study was obtained from an oil separation tank in a petroleum refinery facility. The optimal combination of factors for oil recovery was 10 C/N ratio, 35°C, 1:4 (sludge:water), and inoculum concentration of 4%. In this case, the total extractable organics (TEO) recovered was 86% at the laboratory scale (Yan *et al.*, 2012). Also, these authors did an oil recovery pilot study with the optimal formula mentioned before, and the TEO recovery was between 82% (Yan *et al.*, 2012). They claimed that their study was the first to investigate the oil recovery from oil sludge using microorganisms and the first report on oil recovery from oil sludge on field pilot-scale. However, Joseph and Joseph (2009), also evaluated the oil recovery from oil sludge using biosurfactant-producing *Bacillus* strains with an oil recovery efficiency of 97%.

Interestingly, Pornsunthorntawee et al. (2008) showed more oil recovery efficiency using surfactin and rhamnolipid than three synthetic surfactants (Tween 80, sodium dodecylbenzenesulfonate (SDBS), Alfoterra 145-5PO). Sand mixed with motor oil was used as the sludge matrix. Surfactin and rhamnolipid had an oil recovery rate of 62% (± 0.03) and 57% (± 0.58), respectively. In the case of the synthetic surfactants, the oil recovery rates for Tween 80, SDBS, and Alfoterra 145-5PO were 53% (± 0.01), 51% (± 0.19), and 55 (± 0.48), respectively (Pornsunthorntawee *et al.*, 2008). The findings of this study are consistent with those of Lai et al. (2009) who found that rhamnolipids and surfactin had a higher TPH removal efficiency from contaminated soil compared to Tween 80 and Triton X-100. For example, when the soil was contaminated with 9000 mg $TPH \cdot kg^{-1}$, the percentages of removal efficiency were

63% for rhamnolipids, 62% for surfactin, 40% for Tween 80, and 35 % for Triton X-100. Wei et al. (2005) mentioned that biosurfactants can be used mixed with other (bio)surfactants and co-solvents to enhance their performance.

Compatible surfactants mixtures are widely used in the preparation of pharmaceuticals, detergent and cosmetics due to their better surface activity compared to the use of a single surfactant (Ghosh, 2001; Chatterjee *et al.*, 2006). Also, surfactant mixtures have been applied in EOR processes to increase solubilisation of the oil (Ghosh, 2001; Chatterjee *et al.*, 2006; Hirasaki *et al.*, 2011; Sahu *et al.*, 2015). All possible combinations of surfactant mixtures have been proposed regarding their ionic nature (Chatterjee *et al.*, 2006). The combinations include non-ionic/non-ionic, cationic/anionic, cationic/non-ionic, and anionic/non-ionic, where an antagonistic or synergistic effect can occur depending on the nature and properties of the involved surfactants (Antón *et al.*, 2008). For example, this effect can determine the final CMC of the mixture. Therefore, three alternatives can occur: an average CMC between surfactants (no effect), and a CMC less (synergism) and CMC higher (antagonism) than the CMCs of each surfactant (Rosen and Kunjappu, 2012).

Synergism in the mixture is based on the attractive interactions between surfactants. These interactions can occur due to the Van der Waals attraction of hydrophobic groups in the surfactants or the electrostatic attraction of charged hydrophilic groups in the case of ionic surfactants (El-Batanoney *et al.*, 1999; Chatterjee *et al.*, 2006). High levels of synergism are observed in ionic and non-ionic surfactant mixtures (Rosen and Kunjappu, 2012). Also, an improvement in colloidal stability by reducing interfacial tension using ionic and non-ionic surfactants in a combination has been observed (Almgren *et al.*, 1996; Feitosa and Brown, 1998). In addition, the mixture of two surfactants can create a new compound with characteristics that are different to the features of each surfactant separately (Antón *et al.*, 2008). Moreover, Chatterjee et al. (2006) mentioned that the modification of the surfactant mixture ratio could influence the CMC, and a 1:1 surfactant mixture ratio can be a breakpoint between antagonistic and synergistic effects in a surfactant mixture. For example, the mixture of two non-ionic surfactants (Brij 58 and Tween 20) showed an increase of the synergistic interaction (e.g. decreasing the CMC value) at increasing concentrations of Brij 58 until a 1:1 ratio to Tween 20 was reached. On the contrary, higher ratios than 1:1 showed an antagonistic interaction (increasing the CMC) (Chatterjee *et al.*, 2006). Also, El-Batanoney et al. (1999) stressed the importance of the 1:1 ratio. In this case, when a non-ionic (fatty stearic acid amide and diethanolamine) and an anionic (dodecyl benzene sulfonic acid) surfactants were mixed,

the lowest interfacial tension value was obtained at a 1:1 surfactant mixture ratio. The interaction is not strong in this situation as the two surfactants has a negative β parameter (Rosen, 1989). The parameter β is used to evaluate the molecular interaction (nature and strength of the interaction) between surfactants in a mixture. This parameter is related to the Gibbs free energy change of the mixture (ΔG_{mix}). A positive β value shows less attraction between surfactants (antagonism), whereas a negative value indicates greater attraction (synergism) (Rosen and Kunjappu, 2012).

The reason for adding non-ionic surfactants into the mixture with other types of surfactants is that the non-ionic surfactants are compatible with the majority of all surfactants, due to their non-charged state (Rosen and Kunjappu, 2012). In addition, this type of surfactants is resistant to hard water and high concentrations of electrolytes (Rosen and Kunjappu, 2012). Indeed, knowing the nature and CMC of surfactants is important when formulating surfactant mixtures. Tadros (2005a) and Antón et al. (2008) recommended the combination of a surfactant of lipophilic nature with one with hydrophilic nature in the formulation of surfactant mixtures. This event will enhance the action of the mixture by guaranteeing partition of the former surfactant into the oil and the latter surfactant into the water (Antón *et al.*, 2008). Also, Rosen and Kunjappu (2012) proposed the use of di(2-ethylhexyl) sulfosuccinates and polyoxyethylene (POE) surfactants such as TX100 and TX114 for an optimal demulsification of W/O emulsions.

2.12. Summary

This review discussed the characteristics and sources of oil sludges. The uniqueness of the these wastes was pointed out by discussing the large variety of samples that can be found not only on a large scale (oil refineries) but also on a lesser scale in which oil sludges can be produced in the motor engines and machines. Due to the several sources of oil sludges, a significantly high amount of this waste is generated. For example, around 18,000 tonnes of tank bottom oil sludge are generated in an oil field in Oman per year (Al-Futaisi *et al.*, 2007). Therefore, there are various treatments (physicochemical or biological) to treat these sludges. This chapter presented an overview of these treatments mentioning the advantages and disadvantages. According to the European Parliament (2008), an approach for treating these sludges is the recovery and reuse of the oil from the sludge. Particularly, the use of surfactants

in oil sludge washing is a potential pretreatment method because it is rapid and cost-effective, and also it can be applied to treat high volumes of waste. Microwave irradiation is an alternative efficient method to recover the oil, but the costs are much higher due to the equipment used. In fact, this disadvantage hampers its application on a large scale. In addition, the application of a biological method such as landfarming or phytoremediation can be time-consuming.

Since co-solvents can be added in oil sludge washing to enhance the oil recovery, it is necessary to find alternative co-solvents that are more benign to the environment. Also, it can be inferred from the literature review that the amount of co-solvent used in the oil sludge washing is much less than the solvent extraction itself because the main component in the oil sludge washing is the surfactant solution.

Finally, there is a need to study the performance of different surfactants in the OSW by assessing the effect of surfactant concentration and application ratio to the sludge. Also, very little is known about the use of the surfactant EOR method in oil sludges from other sources (e.g. oil/water separators and oil drilling sludges), except for the oil tank bottom sludges.

Chapter 3 - Characterisation of the oil sludges and surfactants used

3.1. Introduction

Chapter 2 presented a detailed review of the literature about the current treatment strategies of the oil sludges. It was mentioned that the chosen method should be based on the 3 R concept which includes the **r**eduction, **r**e-utilisation, and **r**ecycling of the waste (Sakai *et al.*, 2011). Also, the European Community have addressed the importance of the prevention, recovery, and reuse of waste oils (European Parliament, 2008). Therefore, the most appropriate approach the oil recovery because the recovered oil can be reused as feedstock for fuel production, and the burden of hydrocarbon contamination can also be reduced. To date, the oil recovery treatments used are centrifugation, pyrolysis, electro-demulsification, microwave and ultrasonic irradiations, freeze/thaw, solvent extraction, froth flotation, surfactant EOR. It was mentioned that centrifugation, pyrolysis, electro-demulsification, microwave and ultrasonic irradiations had higher energy consumption to achieve the demulsification needed to recover the oil. Therefore, their application can be compromised at a large scale due to the high costs. Moreover, freeze/thaw, electro-demulsification, ultrasonic irradiation, and froth flotation are still at a laboratory scale. Regarding the surfactants, these compounds were used to improve the oil recovery in the centrifugation, electro-demulsification, microwave irradiation, and froth flotation methods. In fact, surfactants are important in the oil recovery due to their unique amphiphilic nature (hydrophobic and hydrophilic parts) which can be used to demulsify the W/O emulsion present in the oil sludges. Also, this method has been applied at a large scale, and no complex operations or machines are required. For these reasons, surfactant EOR has been selected in this thesis as the approach for the treatment of oil sludges. One surfactant EOR method known as oil sludge washing (OSW) has been recently applied in the treatment of oil sludges. However, little is known about the influence of the surfactant type, concentration and application ratio to the oil sludge in the oil sludge washing. Moreover, there is a need to test the efficiency of this method in different types of oil sludges.

Oil sludge washing (OSW) was the selected protocol to recover the oil. This method is analogous to the soil washing process, and it has been recently implemented in oil sludges. This process has the surfactants as the key component in the washing solution. Therefore, this

chapter presented a detailed analysis of the surfactants and oil sludges used in the oil sludge washing (OSW) experiments in the next chapters of this thesis.

Before implementing the OSW protocol, it is important to assess the characteristics of the surfactants such as critical micelle concentration (CMC), surface activity and micelle size of surfactants. These features are related to the performance of surfactants in the oil recovery. Schramm and Marangoni (2000) stated that the determination of CMC is crucial in the petroleum industry because the concentrations higher than the CMC favour the enhanced oil recovery. In this case, the presence of micelles can decrease the interfacial tension between oil and water and favour the solubilisation of oil into the micelle core. By knowing the CMC, all surfactants can be evaluated equally with the surfactant concentrations normalised to the CMC (Deshpande *et al.*, 1999; Zhang *et al.*, 2011a).

The surfactants used in this study were Tween 80 (T80), sodium dodecyl sulphate (SDS), Triton X-100 (TX100), rhamnolipid (RL), and Triton X-114 (TX114). The physicochemical characteristics of these surfactants are shown in Table 3.1, the chemical structures of the surfactants are shown in and Figure 3.1.

Table 3.1. Physicochemical characteristics of the selected surfactants for the oil sludge washing.

SURFACTANT	IONIC STATE	CHEMICAL FORMULA [7]	MW [1]	MICELLE [2]/ Agg. [3]	HLB [4]	CMC (mM) [5]	ST [6]	REFERENCES
***Tween 80 (T80)*. Polyoxyethylene (20) sorbitan monooleate. Polysorbate 80**	Non-ionic	$C_{64}H_{124}O_{26}$	1310	10.7/60	15	0.011	38	Hillgren et al. (2002), Yuan et al. (2007), Patist et al. (2000), Kothekar et al. (2007)
Sodium Dodecyl Sulphate (SDS)	Anionic	$C_{12}H_{25}NaO_4S$	288	3.5-4.0/60-70	40.0	7-10	35	Tadros (2005a), Yuan et al. (2007), Urum and Pekdemir (2004)
***Triton X-100 (TX100)*. Polyethylene glycol *p*-Octyl phenol ethoxylate. Mono 30**	Non-ionic	$(C_2H_4)_nC_{14}H_{22}O$	625	7.5/100-155	13.5	0.17-0.3	31	Yuan et al. (2007), Li et al. (2000), Arnold and Linke (2007)
Rhamnolipid (RL)	Non-ionic	$C_{32}H_{58}O_{13}$	546	50-250 [3]/ –	9.5	0.0092-0.42 (5-230 $mg \cdot L^{-1}$)	28	Torres et al. (2011), Urum and Pekdemir (2004)
***Triton X-114 (TX114)*. Polyethylene glycol *tert*-octylphenyl ether**	Non-ionic	$(C_2H_4O)_nC_{14}H_{22}O$	537	10-15 [4]/ 62	12.4	0.2-0.35	29	Xu (2012), Hinze and Pramauro (1993), Arnold and Linke (2007)

[1] MW (Molecular Weight): $g \cdot mol^{-1}$.
[2] Micelle size: Diameter in nanometers (nm). For rhamnolipid, this size corresponds to spherical rhamnolipid vesicles commonly generated after the CMC point (Pornsunthorntawee *et al.*, 2009).
[3] Micellar Aggregation Number (Agg.): Number of surfactant monomers per micelle (Schramm, 2000a).
[4] HLB (Hydrophile-Lipophile Balance): This is a value from an empirical scale from oil-soluble to water-soluble (Schramm, 2000b). HLB scale considers values from 0 to 20 for non-ionic surfactants where values less than 9 corresponds to lipophilic surfactants and values greater than 11 refers to hydrophilic surfactants. Most of the ionic surfactants have HLB values greater than 20 (Schramm and Marangoni, 2000).
[5] Critical micelle concentration (CMC) in mM except for rhamnolipid. This value is also given in $mg \cdot L^{-1}$ as it is commonly reported with this unit.
[6] ST (surface tension) reduction in water ($mN \cdot m^{-1}$).
[7] For Triton X-100 and X-114. **n** = average number of ethylene oxide (EO) units per molecule: Triton X-100 (9 – 10) and TX114 (7 – 8).

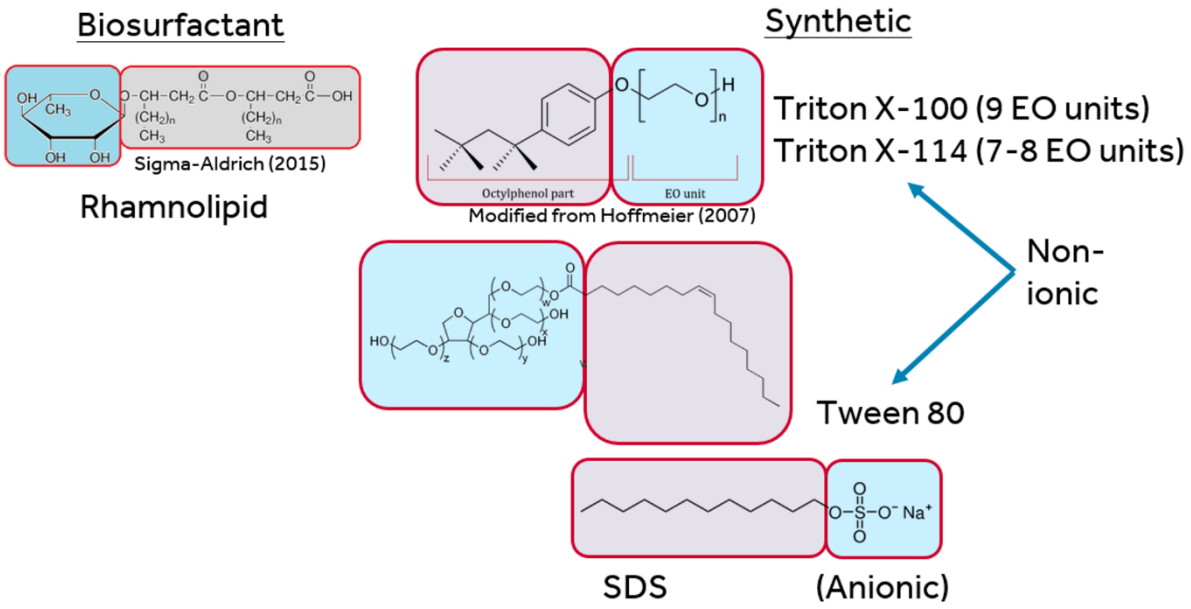

Figure 3.1. Chemical structures of the surfactants used in this study showing the hydrophobic (grey) and hydrophilic (blue) parts for each surfactant. For Triton X-series surfactants, "n" corresponds to the number of EO units (9 for TX100 and 7-8 for TX114). T80 and sodium dodecyl sulphate (SDS) (chemical structures pictures are free licensed by Creative Commons).

The rationale behind selecting these surfactants was based on its ionic charge. There are differences between non-ionic and anionic surfactants. For instance, the CMC and surface tension reduction in water is lower for non-ionic surfactants compared to ionic surfactants (Tadros, 2005a). Moreover, the aggregation number is lower for ionic surfactants, and its micelle sizes are smaller than the non-ionic surfactants (Attwood and Florence, 2012). The surfactants used in this thesis showed these differences (Table 3.1). In addition, a biosurfactant (rhamnolipid) was selected. As mentioned in sections 2.9 and 2.11, these biosurfactants have been used for oil recovery. Zheng et al. (2012) reported that rhamnolipids with butanol as a co-solvent had a 74% of oil recovery from oil sludge. Also, Pornsunthorntawee et al. (2008) have used rhamnolipid to recover oil from a lab-prepared contaminated soil with motor oil matrix. These authors obtained a 55% recovery. Also, the oil recovery using T80 was 50%. A soil washing study reported a crude oil removal from a non-weathered contaminated soil using SDS and RL of 95% for both surfactants. However, if the soil was weathered at 50°C for 14 days, the crude oil removal was 50% (Urum *et al.*, 2004). Although, there are more types of biosurfactants such as glycolipid (*Rhodococcus* sp.) and surfactin (*Bacillus subtilis*), these surfactants were difficult to find commercially. Similar to rhamnolipid, the reason is due to the

high costs involved in the large scale production of these biosurfactants (Makkar and Cameotra, 1999).

Also, TX114 was used in soil washing studies from PAH-contaminated soils. For instance, Zhou and Zhu (2007) found that the desorption percentages of phenanthrene by TX100 and TX114 were 73% and 80%, respectively. TX114 is used in the purification and concentration of membrane proteins by phase separation. Since the cloud point of this surfactant is between 20 to 25°C, the detergent-solubilised proteins separates with the surfactant-enriched phase (Arnold and Linke, 2007). Therefore, TX114 was selected to be used in this thesis to account for the possibility of the recycling of this surfactant by reaching its cloud point. TX100 has a higher cloud point at 65°C, but this surfactant has been used in oil recovery studies as mentioned before.

Dynamic light scattering (DLS) is used for the determination of the particle size in colloidal dispersions. Also, it has been used for CMC determination (Malvern, 2006b; Rosen and Kunjappu, 2012; Topel *et al.*, 2013). The measurement of the size is done by scattering monochromatic light to the micelles. The physical event involved is the Brownian motion that refers to the random movement of the particles in solution. This random motion gives a range of fluctuations in the intensity of the scattered light (Topel *et al.*, 2013). A detector located at a particular angle to the light measures these fluctuations. The constant bombardment of the solvent induces random movement of the particles (Berne and Pecora, 1976). Regarding this principle, large particles diffuse slower than small particles. DLS is a fast and not sample-destructive method (Borgstahl, 2007).

Micelle formation can be detected by abrupt changes in some physical properties of surfactants (Dominguez *et al.*, 1997; Topel *et al.*, 2013). Therefore, tensiometry, conductometry, spectrofluorometry, sound velocity, static light scattering (SLS), and DLS can be used to measure the CMC (Rosen and Kunjappu, 2012; Topel *et al.*, 2013). The most common method is the tensiometry where the du Noüy ring and pendant drop method are used. The first method measures the surface tension with the force or pressure exerted by a ring that is the force required to lift the ring from the surface of the liquid (du Noüy, 1919). On the contrary, the pendant drop method measures surface tension from a collapsing drop with the surfactant solution. This method is used primarily for measuring interfacial tension between two immiscible aqueous solutions (Arashiro and Demarquette, 1999), but it can be used for surface tension measurements (Schramm and Marangoni, 2000; Saad *et al.*, 2011).

The analyses of the oil sludges included the determination of the water and total dry (solid and organic material) contents by the oven dry method. Nuclear magnetic resonance (NMR) was used to confirm the oil and water contents. Also, the trace elements (including heavy metals) and a total EPH determination of the sludges were undertaken.

Briefly, the nuclear magnetic resonance (NMR) is based on the atomic measurement of the nuclei present in the analyte compounds by stimulating these nuclei using a strong magnetic field. The most common elements analysed are ^{1}H and ^{13}C (Ham and MaHam, 2016). Since the nuclei are magnetic charged, the NMR applies a magnetic field to the sample to generate an energy transfer between them (Balci, 2005). The nuclei have a spin quantum number (+½ or -½); the spinning of the charged nucleus generates a magnetic field. This magnetic moment travels along the axis of the spin (Ham and MaHam, 2016). Then, when the spin of the nuclei returns to their basal level, the signal is emitted through the NMR (Balci, 2005). In addition, the relaxation process allows the spin to return to its thermal equilibrium and basal level. Since the relaxation time is slow, there is plenty of time to measure spins. The relaxation can be divided into two processes which are the T_1 longitudinal and T_2 transverse relaxations. The former is related to the return of the thermal equilibrium, and the latter describes the decay of the magnetisation of the spins (Keeler, 2010).

NMR has been used recently as a rapid method to confirm the oil and water content of the oil sludges. This method was selected because NMR does not require a large amount of sample or solvents, and it is a non-sample destructive method (Zheng *et al.*, 2013) compared to other methods such as azeotropic distillation which can use around 200 ml of toluene (Jin *et al.*, 2014). Low-field NMR has been used successfully for the determination of oil and water in oil sludges (Jin *et al.*, 2013; Zheng *et al.*, 2013) and in crude oil-water mixtures (LaTorraca *et al.*, 1998; Silva *et al.*, 2012). For instance, this method showed a good correlation ($R^2 > 0.99$) with the oil and water content data from oil sludges obtained with the azeotropic distillation (Jin *et al.*, 2013; Zheng *et al.*, 2013).

The aim of this chapter is to present the physicochemical description of both oil sludges and surfactants used in this thesis.

3.2. Materials and Methods

3.2.1. Surfactants

RL (90% pure rhamnolipid) was obtained from AGAE Technologies (Corvallis, Oregon, USA). SDS was supplied by BDH Laboratory supplies. T80, TX114 and TX100 were laboratory grade and supplied by Sigma-Aldrich. All concentrations needed for the study were prepared from an intermediate stock solution of 10% (w/v) of SDS and RL, and 10% (v/v) of TX100, T80 and TX114 dissolved in ultrapure water (18.2 MΩ·cm).

3.2.1.1. Determination of micelle size using dynamic light scattering (DLS)

In this study, the size of the micelles was determined by measuring the hydrodynamic diameter using dynamic light scattering (DLS). Since the micelles from the surfactant solution are monomodal (i.e. with one type of shape), monodisperse at higher concentrations than CMC where micelles are mostly present, and spherical (Rosen and Kunjappu, 2012), DLS can be used for determining the size of these particles (Malvern, 2005).

Samples were analysed in a Malvern Zetasizer NANO ZS (Malvern Instruments Limited, UK). The machine had a 4 mW He-Ne red laser at 633 nm and an avalanche photodiode (APD) detector. The sensitivity of the hydrodynamic diameter size detection in the machine ranged from 0.6 nm to 6000 nm. Light scattered from the particles was detected at a 173° angle by a measurement technique known as non-invasive back scattering (NIBS) (Malvern, 2005). In this method, the signal quality required to measure these nanoparticles remains stable while the detection of scattered light is maximised. Therefore, the sensitivity of measurement is high even at low concentrations (Topel *et al.*, 2013). Refractive indexes used for SDS, TX100, T80, RL and TX114 were 1.461, 1.492, 1.4756, 1.33, and 1.48, respectively (Malvern, 2005). Since the samples were highly diluted due to low concentrations to reach the CMC, samples were not coloured and the assumed absorption value used was 0.000. The dispersant used for the surfactants was ultrapure water with a polydispersity index (PDI) and resistivity of 0.23 (±0.05) and 18.2 MΩ·cm, respectively. Count rate for ultrapure water was 29.87 kcps (±1.45) (kilocounts per second). Viscosity and refractive index for the water used

in the analysis were 0.89 cP (1 centipoise (cP) = 1 mPa·s^{-1}) and 1.330, respectively because the tested concentrations of the surfactants were less than 0.1%. Therefore, the viscosity of the sample registered in the machine was the same as the water (Malvern, 2005).

Samples were transferred to polystyrene latex disposable cuvettes (refractive index = 1.590; absorption = 0.010) using a 3 ml sterile syringe connected to a Minisart 0.25-micron syringe filter (Sartorius) by slightly pressuring the plunger to avoid the formation of bubbles that could interfere with the analysis. Filtration is necessary because the sample is extremely sensitive to dust, and the results can be affected (Hoo *et al.*, 2008). Since the analysis is very sensitive to contamination even at a nano-scale, new cuvettes were used for each analysis. Cuvettes were filled up to 10 mm to 15 mm to avoid temperature gradients (Malvern, 2005).

The output of the cumulant analysis gives the mean value for the size (z-average diameter) and the polydispersity index, PDI (a width parameter of the size distribution) (Malvern, 2005). The hydrodynamic diameter was reported by the z-average diameter. This diameter was obtained from the signal intensity, and it was calculated from the translational diffusion coefficient obtained in the data output from the detector of the machine (Borgstahl, 2007). The Stokes-Einstein equation (Equation 3.1) was used for obtaining the real hydrodynamic diameter (micelle size) from this output (Malvern, 2006a).

$$\boldsymbol{d(H)} = \frac{\mathbf{k}\boldsymbol{T}}{\mathbf{3}\boldsymbol{\pi}\eta\boldsymbol{D}}$$

Equation 3.1. Stokes-Einstein Equation.

where *d(H)* is the hydrodynamic diameter, *k* is the Boltzmann's constant (1.3807 x 10^{-23} joules per kelvin, J·K^{-1}), *T* is the temperature (20°C), η is the viscosity of the surfactant solution, and *D* is the translational diffusion coefficient obtained for each sample.

3.2.1.2. Determination of the critical micelle concentration (CMC) by the pendant drop method

The pendant drop was measured with an optical Attension Theta Lite tensiometer. A 1.0 ml Hamilton Gastight syringe was used to take the sample and its plunger was rotated to take and release the pendant drop. The image calibration factor was 1.00 x 10^{-5}. The automatic baseline option of the drop was used. The analysis of the collapsing drop started until the baseline was totally flat, so the drop can be stable by reaching hydrodynamic and mechanical equilibria. These equilibria is reached due to the gravitational force and the surface tension (Song and Springer, 1996). The OneAttension v. 1.8 (Biolin Scientific) software was used to record and analyse the data in a computer. The optical tensiometer had a digital camera attached. The drop was recorded for 10.0 seconds (12 fps, frames per second) capturing a maximum of 121 frames. The surface tension of the drop was analysed with Equation 3.2.

$$\gamma = \frac{\Delta\rho \cdot G \cdot R_0^2}{\beta}$$

Equation 3.2. Surface tension equation used in the pendant drop method (BiolinScientific, 2014).

where, γ is the surface tension, Δρ is the density difference in the air/aqueous solution, *G* is the constant of gravity (9.81 m·s^{-2}), R_0 is the radius of the drop curvature at the apex, and β is the shape factor (BiolinScientific, 2014). β is obtained from the Young-Laplace equations (Figure 3.2) giving the pressure difference in the curved interface of the drop using its principal radii of curvature (Schramm, 2000a). These first order equations are dimensionless (BiolinScientific, 2014). Equation 3.2 was calculated by the software that analyses the pendant drop method data.

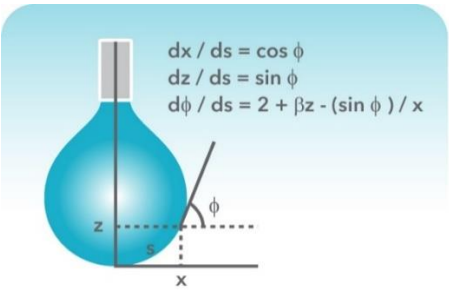

Figure 3.2. Young-Laplace equations and their application in a drop profile from BiolinScientific (2014).

Values of surface tension per concentration were the weighted average of three different means (Clarke and Cooke, 1992) measured in the 10 seconds time-lapses. The CMC was the point when an abrupt change in the surface tension was evidenced (Topel *et al.*, 2013).

The CMC point was determined by obtaining the intercept point between the two regression lines (Yuan *et al.*, 2007). The first line resulted from the decreasing of surface tension before the CMC, and the other regression line was obtained at the stabilisation of surface tension after the CMC as shown in Figure 3.3.

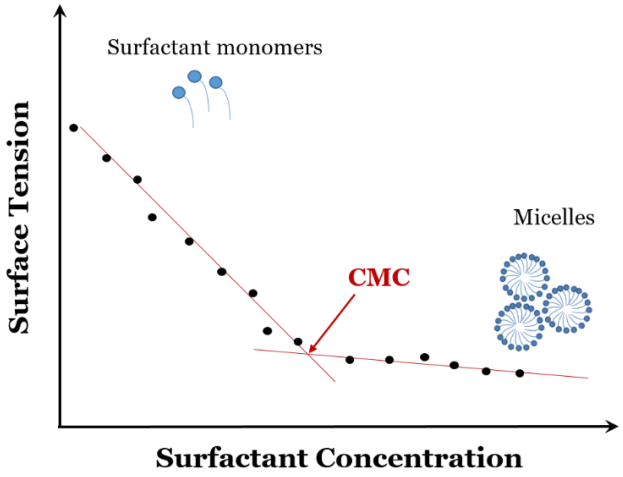

Figure 3.3. Depiction of the calculation of the CMC with the intercept point of the two regression lines.

3.2.1.3. Surface activity of the surfactants by the oil displacement test

This method was used for the determination of surface activity of surfactants by measuring the area of the clear zone after the addition of a surfactant to a drop of oil. 40 ml of deionised water were added to a 9 cm-diameter Petri dish (Rodrigues *et al.*, 2006). Then, 100 µl of used motor oil were dropped, and a thin oil layer was formed on the surface of the deionised water. The surfactant solution (10 µl) was added later to the surface of the oil. PBS (phosphate buffer saline supplied by Sigma-Aldrich) was used as a control (Rodrigues *et al.*, 2006). The maximum area of the clear halo zone was observed under different concentrations of surfactants (Pornsunthorntawee *et al.*, 2008), and the surfactants with a high surface activity had large clear area zones (Rodrigues *et al.*, 2006).

Digital pictures of the clear zone were taken at 30 seconds after the addition of the surfactant (Chandankere *et al.*, 2013). The digital camera used was always at the same distance from the Petri dish by holding the camera in a retort stand with a clamp. The resolution of the pictures was 72 dpi (dots per inch) with a width of 3648 pixels and a height of 2736 pixels. These photos were analysed using the image processing and analysis software, ImageJ (Schneider *et al.*, 2012). Equivalent pixels measured per centimetre were standardised using 20 repetitions. Then, the mean value obtained (pixels per centimetre) was used to calculate the area of the clear zone in cm^2. A two-way analysis of variance was performed on the data with effects of surfactant type and surfactant concentration in the area of the clear halo zone using Minitab 17.3.1 (Minitab Inc.). Also, a *post hoc* Tukey test was done ($\alpha = 0.05$). All the graphs were created using GraphPad Prism 7.01 for Windows (GraphPad Software, Inc.).

3.2.2. Oil sludges

Oil sludge samples were stored in amber glass sealed containers at 4°C to avoid volatilisation of light hydrocarbon compounds and photodegradation. This type of container is the best option for oil collection. Other options such as metal and plastic containers are not recommended because these materials can react with the oil; especially phthalates that can be leached from the plastic to the oil (Peters *et al.*, 2005).

3.2.2.1. Water and total dry matter content of the oil sludges

The water and dry matter contents were analysed according to the protocol from the European Committee for Standardisation (CEN) (EN12880, 2003). The dry matter content included the dried solid and organic material contents. Briefly, an empty crucible was dried at 105°C for 30 minutes, and it was allowed to cool down in a desiccator. The weight of the cooled empty crucible was measured (M_c). Then, the oil sludge samples (5 g) were added to the crucible, and the weight of the crucible with the sample was determined (M_{cs}). The crucible with the samples was dried at 105°C for 24 hours. After, the crucible was allowed to cool down, and its weight (M_d) was recorded until a constant mass was achieved. Equation 3.3 and Equation 3.4 (EN12880, 2003) show the calculations for water and dry matter contents, respectively.

$$Water\ content\ (\%) = \frac{M_{cs} - M_d}{M_{cs} - M_c} \times 100\%$$

Equation 3.3. Water content (%) of the oil sludge sample.

$$Dry\ matter\ content\ (\%) = \frac{M_d - M_c}{M_{cs} - M_c} \times 100\%$$

Equation 3.4. Dry matter content (%) of the oil sludge sample.

Since the calculation of dry matter content included the total dried residue (oil and solids), the solid content was determined by burning the 105°C-dried samples at 550°C in a muffled furnace for 30 minutes. Equation 3.5 was used to calculate the solid content of the oil sludge (Taiwo and Otolorin, 2009).

$$Solid\ content\ (\%) = \frac{M_{sc}}{M_{os}} \times 100\%$$

Equation 3.5. Solid content (%) of the oil sludge sample.

where M_{sc} corresponds to the mass of residue after burning at 550°C and M_{os} is the original mass of oil sludge. By knowing the solid content, the organic material content is the mass lost in the burning at 550°C (Zubaidy and Abouelnasr, 2010). This mass can be calculated by subtracting the solid content (Equation 3.5) from the dry matter content at 105°C (Equation 3.4).

3.2.2.2. Analysis of trace elements in the oil sludges

Samples were treated by *aqua regia* digestion. Oil sludge (1.5 g) was air dried in a fume cupboard for seven days at room temperature (Chen *et al.*, 2015), and it was transferred to a 100 ml Kjeldahl digestion tube. Four glass balls (1.5 mm-2mm diameter) were added to the tube. Then, 10.5 ml of concentrated AnalaR grade hydrochloric acid were added followed by 3.5 ml of concentrated AnalaR nitric acid which was poured gradually to avoid foaming; both acids were supplied by Sigma-Aldrich. The Kjeldahl tubes were left overnight in a fume cupboard covered by a glass bubble of marble. After, the tubes were placed in a digestion block and heated very cautiously to 50ºC. The temperature of the digestion block was increased gradually to 140ºC at a rate of $5ºC \cdot min^{-1}$ checking continuously that non-excessive foam was formed. Samples were left at 140ºC for 2 and a half hours and then removed from the block to cool down. Samples were then filtered using a Whatman Grade 540 quantitative filter paper (Sigma-Aldrich) by washing the glass bubble, the sample and the filter with 0.5 M nitric acid into a 100 ml volumetric flask. The final volume of 100 ml was achieved with the further addition of 0.5 M nitric acid. Samples were then diluted tenfold with 18.2 MΩ·cm ultrapure water.

These prepared samples were analysed using inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 7300 DV) and quantified with the WinLab32 ICP Continuous software (PerkinElmer). Multi-element and arsenic standards dissolved in *aqua regia* mixture and ultrapure water were used for calculation of the concentrations. Trace elements analysed with their wavelengths (nm) included aluminium (Al, 396), arsenic (As, 188.979), barium (Ba, 455), calcium (Ca, 317), cadmium (Cd, 228.802), cobalt (Co, 230.786), chromium (Cr, 205), copper (Cu, 324), iron (Fe, 259), potassium (K, 766), lithium (Li, 670.784), magnesium (Mg, 279), manganese (Mn, 257), sodium (Na, 589), nickel (Ni, 231), lead (Pb, 2220), strontium (Sr, 407), and zinc (Zn, 213). As, Cd, Co, Cr, Cu, Ni, Pb, and Zn are

considered as potentially toxic elements (PTEs) (Hawkes, 1997; Shaheen *et al.*, 2016). Since the type of digestion used in the study did not dissolve any silicates in the samples, the results obtained here are not total metal values. Therefore, the metals analysed are *aqua regia* soluble.

3.2.2.3. Nuclear magnetic resonance (NMR) of oil and water contents

All NMR spectra were recorded with a Bruker Avance III spectrometer operating at a Larmor frequency of 500 MHz (11.75 T; high field-NMR) and equipped with Broadband Observe (BBO) High-Resolution solution probe. The oil sludge sample with fixed volume of 200 µl was transferred through a Pasteur pipette with long tips (Fluorochem) equipped with a glass wool plug to a standard 5mm Norell S 5-400-7 NMR tube. This volume was sufficient to ensrue that the whole sample fit inside the active space of the radiofrequency (RF) coils. The maximum possible homogeneity of the magnetic field was achieved by using a "shimming standard" of oil dissolved in 0.5 µL deuterated benzene (Sigma-Aldrich). This standard was tested to correct the measurement signal using the absorption frequency of the deuterated benzene, first by "locking" the signal to the parameters of this solvent to guarantee stable and homogenous signal in the sample. Second, the "shimming" is done to ensure that there is a homogeneous magnetic field along the coil where the sample is placed. Once the shims were optimised with the "shimming standard", no shimming and locking was performed on the oil sludge sample (Claridge, 2009).

The Carr-Purcell-Meiboom-Gill (CPMG) sequence was used to measure the T_2 relaxation times. The 90° pulse was 10 µs at the power level of 17 W and the fixed echo time was 0.26 ms (milliseconds). However, after a fixed number of echo loops (e.g. 5 loops x 2 = 10^{th}), not the spin echo but the single FID signal (half of the spin echo) was recorded and Fourier transformed into 1D NMR spectrum. This procedure was repeated 128 times in the range of the echo loops (from 1 until 8192, unequally spaced) to fully cover the T_2 signal decay associated with oil and water. A total of 8 transients (number of executions of the pulse) were recorded and averaged into each FID/spectrum. The relaxation delay of 15 s was used to guarantee a full relaxation of the spins.

The phase and a baseline correction were applied to each 1D NMR spectrum before integration in the wide spectral range to cover fully the broad oil and water resonances. The series of the integrals as a function of the echo time formed the final T_2 decay curve for each sample. These output data were extracted using the TopSpin v. 3.5 pl 5 (Bruker).

The T_2 decay data were further analysed in Microsoft Excel (2013) by fitting an exponential function constructed from the two components (oil and water) and the background constant. This fitting allowed the determination of the water and oil fractions because the water peak had a slow relaxation (e.g. 1,000 ms) compared to the rapid relaxation of oil (e.g. 1 ms). Consequently, both distributions (T_1 and T_2) are bimodal (LaTorraca *et al.*, 1998). The oil and water contents were calculated as a percentage of the respective amplitudes of the fit components. Also, some oil and water standard mixtures were tested before the analysis of the oil sludges. The relative experimental errors and R^2 values of the NMR data versus the expected percentage values of both oil and water standards were calculated to validate the method. Moreover, the percentage difference between the 1D proton and T_2 decay data was calculated to confirm further the reliability of the NMR method in assessing the oil and water contents from oil sludges.

3.2.2.4. EPH extraction from oil sludge

Acetone and hexane were high-performance liquid chromatography (HPLC) grade, and these solvents were supplied by Fisher Scientific. All material was cleaned by rinsing with hexane. After, the materials were soaked for 12 h in water with alkaline lab detergent (supplied by Decon Laboratories Ltd.). Then, these materials were washed with tap water, rinsed with deionised water, and dried in the oven at 100°C for 12 h (USEPA, 1996). Lab material was rinsed again with hexane before the experiment. The oil sludge (1 g) was mixed with a 10 ml acetone:hexane solution (1:1, v/v) (Reimers, 2001) at 1:10 ratio. This combination of solvents was intended to obtain the PHCs in the top hexane layer as this solvent is more hydrophobic compared to acetone. Acetone and hexane have polarity indexes of 5.1 and 0.1 (Harris, 2015). 1-chlorooctadecane and *o*-terphenyl mixture (200 µl) supplied by Sigma-Aldrich were added as surrogate standards. In this thesis, surrogate standards were used to test the extraction efficiency, so the standards were added at the beginning of the extraction. The blank consisted of 1 g of ultrapure water (18.2 MΩ·cm) mixed with sand (50-70 mesh particle size). Vials were

placed in an ultrasonic bath (Guyson International Ltd., UK) filled with hot tap water and sonicated for 15 minutes (Reimers, 2001). Samples were then shaken on a Stuart roller mixer SRT9D (Bibby Scientific Ltd.) for 60 minutes at 60 rpm. After that, deionised water (4 ml) was added to separate hexane layer from acetone layer. Vials were frozen at -25°C to separate water from the hexane, which was then evaporated under a gentle nitrogen stream to 1 ml at 40°C in a Techne sample concentrator with a Dri-Block DB-3 (Bibby Scientific Ltd.). Due to the high concentration of oil, the samples were diluted (1:10) in hexane before the solid-phase extraction (SPE) clean-up.

3.2.2.5. Solid-Phase Extraction (SPE) clean-up and separation of aliphatic and aromatic compounds

Gas chromatography grade silica gel (60 Å; particle size 63 – 200 µm), sand (50-70 mesh particle size) (Sigma-Aldrich) and anhydrous sodium (Fisher Scientific) were used as sorbents for the stationary phase of the SPE. Since the silica gel and sodium sulphate are polar, the SPE technique applied was a normal-phase chromatography for the aliphatic/aromatic separation and clean-up. The silica gel and anhydrous sodium sulphate were activated before the clean-up. First, these materials were ultrasonicated with hexane for 30 minutes. Then, the excess of hexane was removed, and remnants of hexane were allowed to evaporate in a fume cupboard. Both sorbents were heated for 16 hours at 130°C, and then placed into a desiccator during cooling. Silica gel was then deactivated by adding 3% of deionised water by weight. This deactivation was done to improve the definition of the chromatographic zones in the fractionation of PAHs (Cahnmann, 1957). Both silica gel and sodium sulphate were maintained in a desiccator until clean-up. Sand was activated in an oven at 400°C for 8 hours.

Silica gel (1g), 0.5 g of anhydrous sodium sulphate and 1 g of sand were added in this order to a 6 ml polypropylene SPE cartridge with a polyethylene frit of 20 µm (Supelco). After the SPE tube was prepared, it was attached to a Visiprep^{TM} vacuum manifold (Supelco). The vacuum was adjusted to approximately 254 mm Hg. The cartridges were conditioned with 6 ml of hexane. The samples (0.5 ml) were added to the cartridge, and the aliphatic fraction was eluted with 3.5 ml of hexane, followed by the aromatic fraction which was eluted with 9 ml of 3% of isopropanol in a hexane solution. Both eluents were then evaporated under a gentle nitrogen stream to 1 ml at 40°C.

3.2.2.6. EPH analysis by gas chromatography-flame ionisation detection (GC-FID)

The WSS sludge sample was the first sludge obtained for this research. At that time, the GC-FID protocol used was based on Christensen and Tomasi (2007). The extracted and cleaned samples were analysed using an Agilent 6890 gas chromatograph with a flame ionisation detector (FID). An SPB-5 GC capillary non-polar column (30 m, 0.32 mm, and 0.25 μm) fabricated on 5% diphenyl and 95% siloxane (Sigma-Aldrich) was used. The average linear velocity of the flow in the column was 55 $cm \cdot s^{-1,}$ and the nominal initial flow was 3.0 $ml \cdot min^{-1}$ of helium at a pressure of 1.91 bars. Injection volume and injection speed were 1 μl and 50 $\mu l \cdot s^{-1}$, respectively, in a splitless mode. The autosampler injection method included: injection with a 10 μl fixed needle autosampler glass syringe (Thermo Scientific), two pre-cleaning steps with acetone and one with hexane, and one cleaning step extra with the sample to condition the syringe. After sample injection, the syringe was cleaned one time with acetone and twice with hexane. The total inlet flow was 72.8 $ml \cdot min^{-1}$. Helium was used as a carrier gas, and its flow rate was 3 $ml \cdot min^{-1}$. The make-up gas (nitrogen) flow rate was 35 $ml \cdot min^{-1}$. The air and hydrogen flows were 350 $ml \cdot min^{-1}$ and 35 $ml \cdot min^{-1}$, respectively. The inlet and detector temperatures were 280°C and 320°C, respectively. The initial oven temperature of the column was 45°C for 2.5 minutes. Then, the temperature was ramped to 320°C at a rate of $20°C \cdot min^{-1}$. In the end, this temperature was held for 10 minutes. The total running time was 26.5 minutes (Christensen and Tomasi, 2007). A total petroleum hydrocarbon (TPH) and polynuclear aromatic hydrocarbons mixtures (Sigma-Aldrich) were used as the aliphatic and aromatic standards, respectively.

This method from Christensen and Tomasi (2007) consisted in the measurement of the whole TPH group. As mentioned on Chapter 2 (Section 2.2), the TPH includes the sum of volatile petroleum hydrocarbons (VPHs) and extractable petroleum hydrocarbons (EPHs). VPHs are divided into one aliphatic fraction of C_5-C_{12} compounds and one aromatic fraction (C_9-C_{10}), and EPHs are referred to the C_9-C_{18} and C_{19}-C_{36} aliphatic fractions, and the C_{11}-C_{22} aromatic fraction (TNRCC, 2001; MADEP, 2004). However, since it was not possible to detect most of the VPH fraction from C_5 to the C_9 compound inclusive due to the sensitivity of the GC-FID (0.5 $mg \cdot l^{-1}$), it was decided to use the method from the Massachusetts Department of Environmental Protection (MADEP, 2004) for the other sludges (ODS, STS, RS, and NSC). This method is specifically aimed to detect and calculate the light (C_9-C_{18}) and heavy (C_{19}-C_{36})

aliphatic fractions and the aromatic hydrocarbons (C_{11}-C_{22}) in terms of extractable petroleum hydrocarbons (EPH). However, in this study, the light aliphatic fraction was calculated from the C_{10} compound because C_9 was not detected in the GC-FID as mentioned before. Therefore, the PHCs were reported in terms of EPHs.

In the MADEP method for EPH compounds (2004) the inlet and detector temperatures were 285°C and 320°C, respectively. The total inlet flow was 55.6 ml·min^{-1}. The make-up gas (nitrogen) flow rate was 25 ml·min^{-1}. The air and hydrogen flows were 400 ml·min^{-1} and 30 ml·min^{-1}, respectively. The oven temperature was 60°C held for 1 minute, ramped to 290°C at a rate of 8°C·min^{-1}, and held for 6.75 minutes. The total running time was 36.5 minutes. An EPH aliphatic hydrocarbons and polynuclear aromatic hydrocarbons mixes were used as calibration standards (Sigma-Aldrich).

The chromatograms were analysed using the OpenLab CDS Chemstation Edition software, Version C.01.07 (Agilent Technologies). Three oil hydrocarbons fractions were evaluated: C_{10}-C_{18} and C_{19}-C_{36} aliphatic, and C_{11}-C_{22} aromatic fractions according to the method from MADEP (2004). A total EPH concentration was obtained in each sample (i.e. a sum of all the three fractions).

A two-way analysis of variance was performed on the data with effects of the sludge type and hydrocarbons fractions using Minitab 17.3.1 (Minitab Inc.). All the graphs were created using GraphPad Prism 7.01 for Windows (GraphPad Software, Inc.).

3.3. Results

3.3.1. Surfactants

3.3.1.1. Determination of the size of the micelles

Table 3.2 shows the Z-average values (hydrodynamic diameters) of the micelle sizes for SDS, T80, TX100, TX114, and RL. In this study, DLS was originally intended for determining the CMC. However, it was not possible to use it for this purpose because DLS is very sensitive to heterogeneous samples. For these reasons, DLS was only used to measure the size of the micelles at surfactant concentrations higher than the CMC point to assure monodispersity of the sample (i.e. homogeneous presence of micelles after CMC). When the samples were analysed at lower concentrations than CMC, the polydispersity index was high because the Zetasizer machine was detecting only the sample background noise of non-micelle particles, aggregates and dust. In fact, the PDI is highly sensitive to the presence of this background noise (Kaszuba *et al.*, 2007).

Table 3.2. Micelle sizes (hydrodynamic diameters) of SDS, T80, TX100, TX114, and RL obtained by DLS.

Surfactant	Concentration (mM)	Z-average (nm)	PDI*
SDS	14	3.61 (±0.06)	0.19 (±0.001)
T80	3	12.1 (±0.17)	0.18 (±0.003)
TX100	1	7.62 (±0.05)	0.12 (±0.02)
TX114	1	14.58 (±0.006)	0.16 (±0.01)
RL	0.18	5.83 (±0.67)	0.32 (±0.03)
RL	0.36	11.2 (±0.79)	0.55 (±0.04)

* The polydispersity index (*PDI*) mean and standard deviation (in parentheses) are shown (n = 3). PDI is a width parameter of the size distribution.

The obtained values for SDS, T80 and TX100 micelles were similar to the values previously reported by Bruce et al. (2002) for SDS (3.5 – 4 nm) and by Malvern (2006b) for T80 (10.7 nm) and TX100 (7.5 nm). No reported values were found for TX114. Rhamnolipid is a vesicle-forming biosurfactant (Pornsunthorntawee *et al.*, 2011) and its vesicle size can range between 50 and 250 nm. The formation of the vesicle can depend on the concentration and its number of bilayers (Pornsunthorntawee *et al.*, 2009). Consequently, the variation in the hydrodynamic diameter of RL was evident at two different concentrations, 4CMC (0.18 mM) and 7CMC (0.36 mM) (Table 3.2). Moreover, RL had the highest PDI due to this variation in the size and shape of the micelles.

Figure 3.4 shows the micelle size distribution by intensity for Triton X-100 to illustrate the DLS output. The purple line indicated a high defined peak with 100% monodispersity due to the significant presence of micelles at 1.0 mM, more than three times the CMC. This was the same concentration used for micelle size determination of TX100 (Table 3.2). The red shaded region showed that no micelles were present at 0.1 mM (red line) since these concentrations were below the CMC (0.3 mM). Also, three peaks were obtained confirming the polydispersity of the sample because the background noise (e.g. dust and other non-related particles) was higher as no micelles were present in the sample. Furthermore, some polydispersity was evident at the CMC (green line).

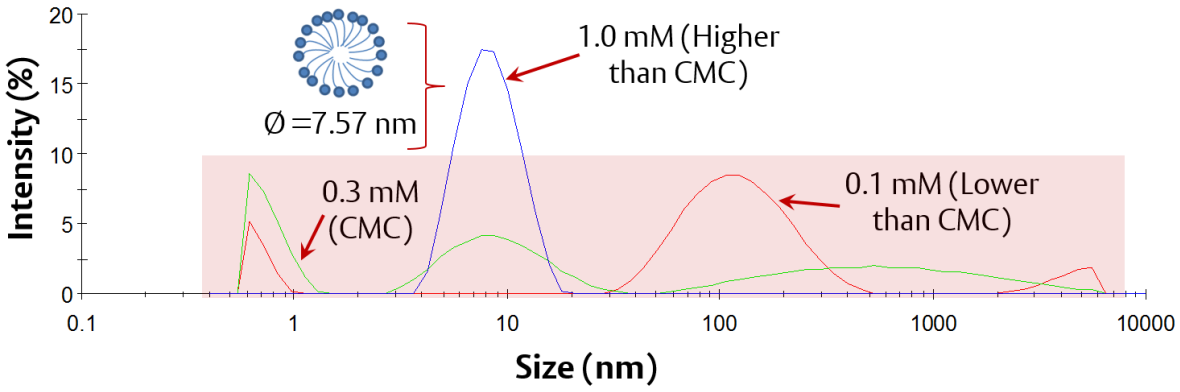

Figure 3.4. Micelle size (hydrodynamic diameter, Ø) distribution by intensity for Triton X-100 at CMC (green line), above CMC (purple line), and below CMC (red line). No micelles were present in the red shaded region.

3.3.1.2. Determination of CMC by the pendant drop method

The pendant drop method consists of the surface tension measurement of a collapsing drop. As the surfactant concentration increases, the drop shape becomes oval in shape due to the reduction in the surface tension. In this case, the area of the liquid is decreasing by the action of the active force or surface tension exerted (Christofi and Ivshina, 2002). For example, this event was evidenced with SDS and Triton X-100 (Figure 3.5).

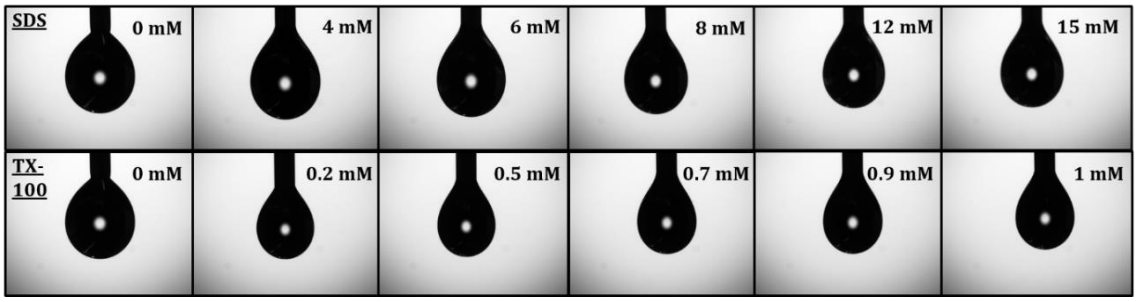

Figure 3.5. Pictures captured by the optical tensiometer for measurement of the surface tension at different concentrations of SDS (top) and Triton X-100 (bottom).

CMC values for the various surfactants obtained by the pendant drop method are shown in Figure 3.6. Non-ionic surfactants (TX100, TX114, and T80) had lower CMC values compared to SDS, an ionic surfactant. RL had the lowest CMC (0.048 mM). The obtained CMC values are in the range of the reported values (Table 3.1), except for T80.

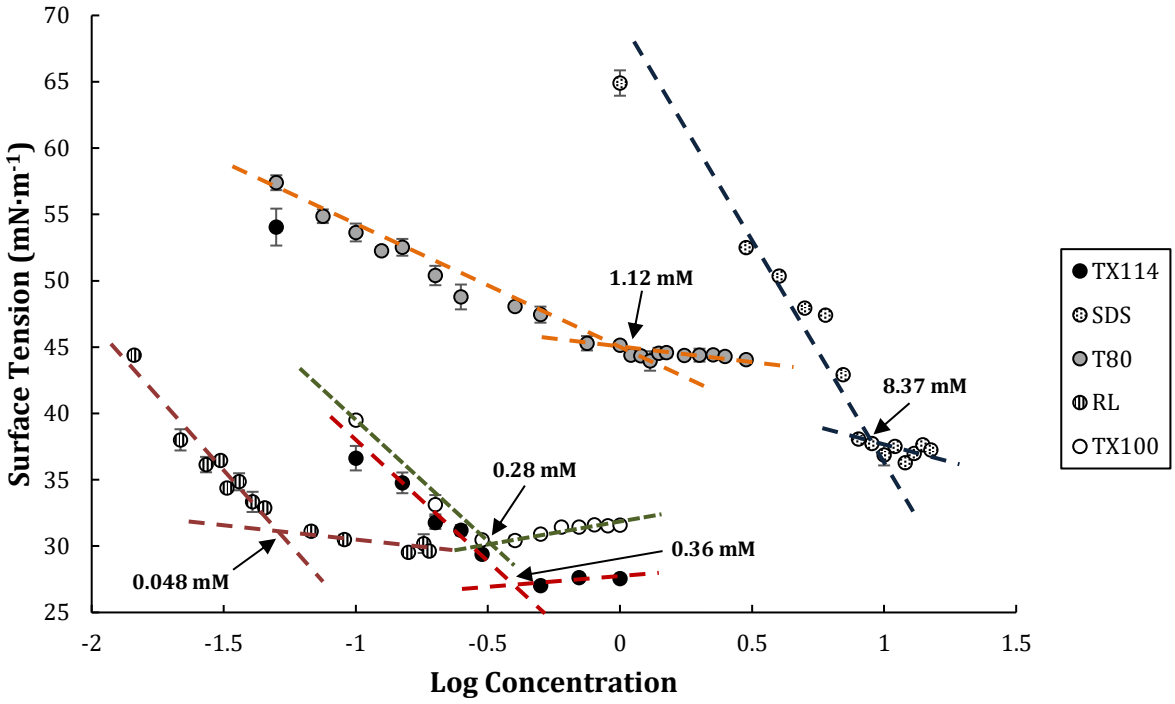

Figure 3.6. CMC values for TX114, SDS, T80, RL, and TX100 obtained by the pendant drop method. The red dashed lines illustrate how the two regression lines were used to calculate the CMC value for all surfactants at their intercept point. The CMC values are indicated by the arrow. The error bars represent the standard deviation.

According to Li et al. (2000), the surface tension of water can be reduced by TX100 to approximately 31 $mN \cdot m^{-1}$ at 24.6°C. Also, the obtained result (Figure 3.6) showed that the surface tension was reduced to 31 $mN \cdot m^{-1}$. The CMC for TX100 was 0.28 mM. For TX114, the surface tension of water was reduced to 27 $mN \cdot m^{-1}$, and the CMC was at 0.36 mM. Dow (2011) have reported a reduction to 29 $mN \cdot m^{-1}$ at CMC (0.29 mM) when TX114 was used. The CMC for SDS was found at 8.37 mM, and the reduction of surface tension in water was 38 $mN \cdot m^{-1}$. Canto et al. (2010) reported a surface tension reduction to 37 $mN \cdot m^{-1}$ at a CMC of 8.58 mM for SDS.

The intercept point of the two regression lines showed that the CMC for T80 was 1.12 mM. Surface tension was reduced to 44 $mN \cdot m^{-1}$, and this value was close to the reported value of this surfactant, 46 $mN \cdot m^{-1}$ (Canto *et al.*, 2010). However, the obtained CMC was 100-fold higher compared to the expected range reported, 0.010-0.012 mM (Table 3.1).

CMC value for RL was 26.31 mg·L^{-1} (0.048 mM). Surface tension reduction was 29 mN·m^{-1}. Sen et al. (2010) and El-Sheshtawy and Doheim (2014) reported that the surface tension could be decreased to 30 mN·m^{-1} and 32 mN·m^{-1}, respectively. Table 3.1 showed that this value is within the range reported in the literature. Variation in the CMC can range from 5 to 200 mg·L^{-1} (Finnerty, 1994; Healy *et al.*, 1996). According to Haba et al. (2003), a source of this wide variation of CMC values can be related with differences in the molecular structure of the rhamnolipid such as composition and ratio of chemical homologs, unsaturation in the chemical bonds, and the length of the aliphatic chains of this biosurfactant.

3.3.1.3. Surface activity of the surfactants by the oil displacement test

A picture of a 1 cm line was taken and analysed using ImageJ (Schneider *et al.*, 2012) to calibrate the standard value of pixels·cm^{-1}. The mean value of this line from 20 measurements was 133 (±1.21) pixels·cm^{-1}. Each concentration was done in triplicate. PBS (negative control) did not generate a clear halo zone (Figure 3.7A). Pictures of the clear halo zone are shown in Figure 3.7B and C.

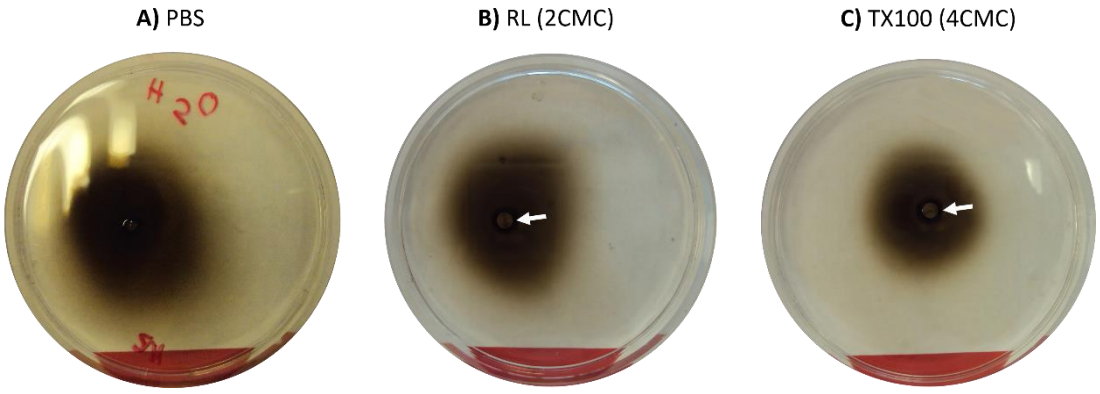

Figure 3.7. Pictures used to calculate the area of the clear halo zone in the image analysing software (ImageJ). A) Negative control with PBS only. B) RL at 2CMC. C) TX100 at 4CMC. The white arrow shows the clear halo zone.

The CMC values used were the same obtained by the pendant drop method (Figure 3.6). Figure 3.8 shows the mean area of clear halo zones obtained for each concentration used (5CMC, 4CMC, 2CMC, CMC, 0.5CMC). According to Morikawa et al. (1993), the oil displacement is generated by the action of the surface pressure of surfactants. This pressure action changes the contact angle at the oil-in-water (O/W) interface.

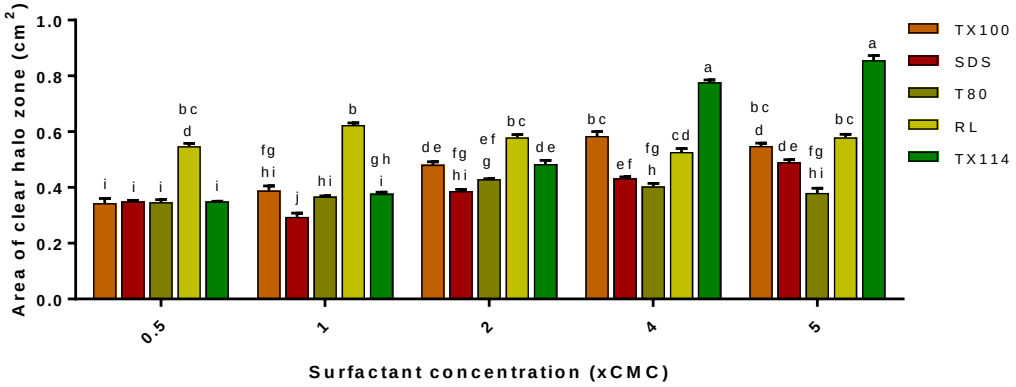

Figure 3.8. Oil displacement test for different concentrations based on the CMC values obtained for TX100, SDS, T80, RL, and TX114. Surfactant concentrations were normalised to the surfactant CMC. Area mean values with the same letter are not significantly different; the comparison of surfactant concentrations with surfactant types was analysed ($p > 0.05$; Tukey's test). The standard error of the mean (SEM) bars are shown ($n = 3$).

A two-way ANOVA revealed a highly significant effect of both the surfactant type and concentration ($p < 0.01$). Consequently, the interaction between these factors was highly significant ($p < 0.01$). A high surface activity of the surfactants can be evidenced by larger areas of the clear zone (Pornsunthorntawee *et al.*, 2008). A *post-hoc* analysis showed that TX114 at 4CMC (0.78 ± 0.01 cm^2) and 5CMC (0.85 ± 0.03 cm^2) had a significantly higher area compared to all the other surfactants and the lower CMC values of TX114. Also, the area with RL had higher areas than the other surfactants (e.g. the highest was 0.62 (± 0.014) cm^2 at 1CMC), and the areas were not significantly different among all RL concentrations (Figure 3.8). TX100 had also significantly higher areas at high concentrations (2, 4 and 5CMC) than

concentrations at low CMCs. The maximum area for TX100 was at 4CMC (0.58 ± 0.03 cm^2). SDS had higher areas at high CMC values compared to Tween 80 with higher areas at low CMC values (Figure 3.8). In summary, RL, TX100, and TX114 were the surfactants with the higher mean areas compared to the other surfactants analysed. RL had higher mean areas at lower concentrations, and TX114 had higher mean areas at higher concentrations compared to TX100, SDS and T80.

3.3.2. Oil sludges

3.3.2.1. Description of the oil sludges used in this study

The oil sludges used in this study were sampled in the United Kingdom. All the sludges have a semi-solid cake form at room temperature. The samples were freshly collected from the field. The WSS sludge was obtained from an oil-water separator in an oil refinery process. The sludge was viscous and black. The ODS sample was an oil drilling sludge. The sludge was viscous and brown. STS and RS were sludges generated at two metal removal processes from waste engine oil with oil additives. These additives can be oxidation inhibitors (iron phosphides and sulfides), and antioxidants and corrosion inhibitors (zinc dithiophosphates and calcium sulfonates) (Bartels *et al.*, 2000). The STS sludge was obtained from gravitational settling, and RS was obtained from the other metal removal process, centrifugation. RS had a more viscous appearance and sludge consistency compared to STS due to the higher presence of sediment in RS. For instance, the solid content for RS was 38% and for STS was 35% (Table 3.3). NSC was obtained from an oil refinery facility where some sediments and water were accidentally mixed to crude oil which generated a sludge consistency. Pictures of the oil sludges can be observed in Appendix A (Table A 1).

3.3.2.2. Physicochemical characteristics of the oil sludges

Table 3.3 contains the water and dry contents. The solid and organic material contents comprised the dry contents. Pictures of the samples before, after heating at 105°C for 24 h (water content) and after heating at 550°C for 30 min (solid content) are shown in Appendix A

(Table A 1). The highest dry matter content was found in the ODS sludge with 87% (±0.02) due to the large quantity of solids (86% ± 0.11) from the drilling mud in this sludge. Consequently, ODS had the least amount of water content (13% ± 0.02). NSC had the least content of dry matter and solid content (1% ± 0.07) since this sludge had the highest dried organic material content (39% ± 2). The NSC sample had a lower amount of solids left after heating at 550°C compared with the other samples. This organic material content was associated partly with the heavy hydrocarbon content because the sample was burned at 550°C. As Zubaidy and Abouelnasr (2010) mentioned, the mass fraction of oil in the sludge is an approximate value of the organic material content in the sludge phase. Although the water content of NSC was the highest, this value could be overestimated due to the high concentration of C_{10}-C_{18} light hydrocarbons that could be volatilised. WSS had the highest amount of water content with a 47% (±1) and the highest amount of dried oil content (30% ± 2) without including NSC (Figure 3.12). Despite the STS and RS sludges originated from the same source, a paired t-test ($\alpha = 0.05$) confirmed that the water content value was significantly higher for the former than the latter sludge ($p = 0.015$), and the solid content was significantly lower for STS compared to RS ($p < 0.01$). However, the organic material was not significantly different between both sludges ($p = 0.104$).

Table 3.3. Water and dry matter contents (%) of the sludges.

		Dry content	
Sludge	**Water content**	**Solid content**	**Organic material**
WSS	47 (±1)	23 (±0.93)	30 (±2)
ODS	13 (±0.02)	86 (±0.11)	1 (±0.10)
STS	41 (±0.16)	35 (±0.16)	24 (±0.09)
RS	35 (±2)	38 (±0.17)	27 (±2)
NSC	60 (±2)	1 (±0.07)	39 (±2)

The means with the standard deviations (in parentheses) are shown ($n = 3$).

The results for the concentrations in part per million (ppm) of the different trace elements analysed in the sludges are shown in Table 3.4. There were no results for NSC due to

the limitation on the amount of sample which was required to be used mostly for the oil washing experiments.

The WSS sludge had higher levels of most of the analysed trace elements compared to the other sludge samples. In general, the sludges were below the limit of the acceptable standards of landfilling established by the European Union (Kriipsalu *et al.*, 2008). Only the levels were higher than the limit in the WSS sludge for Cr, Cu, Ni, Pb, and Zn. In fact, the latter element was over the limit for the other sludges as well.

Table 3.4. Trace metal elements concentrations (µg·g^{-1} dry matter or ppm) analysed in the oil sludges.

Element	WSS	ODS	STS	RS
Al	1,455 (±9)	506 (±20)	104 (±3)	116 (±1)
As*	2 (±0.24)	1 (±0.11)	0.10 (±0.03)	0.13 (±0.09)
Ba	131 (±7)	85 (±13)	40 (±2)	41 (±5)
Ca	5,811 (±44)	4,369 (±2505)	5,260 (±3033)	11,093 (±160)
Cd*	1 (±0.02)	0.08 (±0.01)	0.02 (±0.01)	0.02 (±0.01)
Co*	7 (±0.18)	0.27 (±0.02)	0.66 (±0.01)	0.21 (±0.01)
Cr*	**85 (±0.44)**	2 (±0.19)	9 (±0.30)	9 (±0.07)
Cu*	**142 (±3)**	8 (±0.08)	7 (±0.20)	12 (±0.80)
Fe	5,912 (±26)	1,536 (±867)	16,146 (±252)	13,915 (±278)
K	436 (±12)	85 (±3)	81 (±5)	116 (±6)
Li	2 (±0.01)	0.80 (±0.01)	0.65 (±0.05)	0.86 (±0.03)
Mg	502 (±5)	220 (±10)	235 (±3)	276 (±9)
Mn	142 (±3)	179 (±3)	23 (±0.47)	21 (±0.41)
Na	869 (±21)	65 (±17)	168 (±16)	241 (±3)
Ni*	**85 (±0.58)**	2 (±0.23)	2 (±0.14)	2 (±0.35)
Pb*	**101 (±0.46)**	45 (±2)	9 (±0.93)	9 (±2)
Sr	35 (±0.33)	93 (±6)	6 (±0.24)	7 (±0.07)
Zn*	**376 (±7)**	**1,683 (±22)**	**3,074 (±1814)**	**6,336 (±85)**

***** These elements are potentially toxic elements (PTEs) (Shaheen *et al.*, 2016).
Values in bold are over the limit of the acceptable standards of landfilling of hazardous waste established by the European Union: As (25 µg·g^{-1}), Cd (5), Cr (70), Cu (100), Ni (40), Pb (50), Zn (200) (Kriipsalu *et al.*, 2008). The mean values with the standard deviation (in parentheses) are shown (n = 3).

To have a standard for comparison, the American Petroleum Institute (API, 1989) reported that the ranges of some heavy metals concentrations in oily sludge from petroleum refineries are: Cr (27-80 ppm), Cu (32-120 ppm), Ni (17-25 ppm), Pb (0.001-0.12 ppm), and Zn (7-80 ppm). Chromium (Cr) was higher in the WSS sludge (84.74 ± 0.44 ppm), compared to the other sludges under these parameters. Similarly, this was the case for Cu and Ni with higher concentrations in WSS (142 ± 3, 85 ± 0.58 ppm, respectively) than the other samples. For Pb and Zn, the concentrations were higher than the range mentioned above; notably Zn in the STS and RS sludges were 3,074 (±1,814) and 6,336 (±85) ppm, respectively. Ca and Fe concentrations were greater than 4,000 ppm. For instance, iron (Fe) concentrations were considerably higher for STS (16,146 ± 252 ppm) and RS sludge (13,915 ± 278) compared to the other sludges. Other studies have found highest concentrations of Fe including 34,500 ppm in sludge from the bottom of an oil storage tank (da Rocha *et al.*, 2010) and 92,179 ppm in an oil refinery sludge (Karamalidis *et al.*, 2008). Other trace elements included Ba, K, Li, Mg, Mn, Na, and Sr. In general, these levels were higher for WSS compared to the other sludges. Calcium was high for all the sludges, ranging from 4,000 to 12,000 ppm; the highest Ca concentration was found in RS (11,093 ± 160 ppm).

3.3.2.3. Oil and water contents in the oil sludge by NMR

Nuclear magnetic resonance was used to confirm the water and oil content of the sludges obtained with the oven-drying method. This method was selected because NMR does not require a large amount of sample or solvents, and it is a non-sample destructive method (Zheng *et al.*, 2013). First, a series of oil and water mixtures with known percentages were assessed to evaluate the method. Figure A. 1 to Figure A. 5 in Appendix A show the 1H spectra of the five different oil and water mixture standards tested. Different peaks for the oil and the water component were identified in each standard.

For the validation of the method, the NMR data was compared with the expected percentage values of both oil and water standards. Two calculations were done, the relative experimental errors of each standard and the R^2 values. Most of the experimental errors were less than 15% which validated the method. Only two relative experimental errors (%) were higher than the 15% threshold (Sivarao *et al.*, 2014). One from the oil 20% value (standard 1)

and another from water 30% (standard 4) in which the relative experimental errors were 16% and 26%, respectively.

Table 3.5. NMR Oil and water mixture standards.

Standard	Oil/Water mixture (%) [1]	Experimental value (%)	Relative experimental error (%) [2]
1	Oil 20%	17	16
	Water 80%	83	4
2	Oil 40%	34	14
	Water 60%	66	9
3	Oil 50%	47	5
	Water 50%	53	5
4	Oil 70%	62	11
	Water 30%	38	26
5	Oil 80%	77	4
	Water 20%	23	14

[1] Expected percentage values.
[2] $Relative\ error = |(Experimental - Expected)/Expected| \times 100\%$.

Also, a good linear correlation was observed between the expected oil or water contents and the contents obtained by NMR ($R^2 = 0.990$).

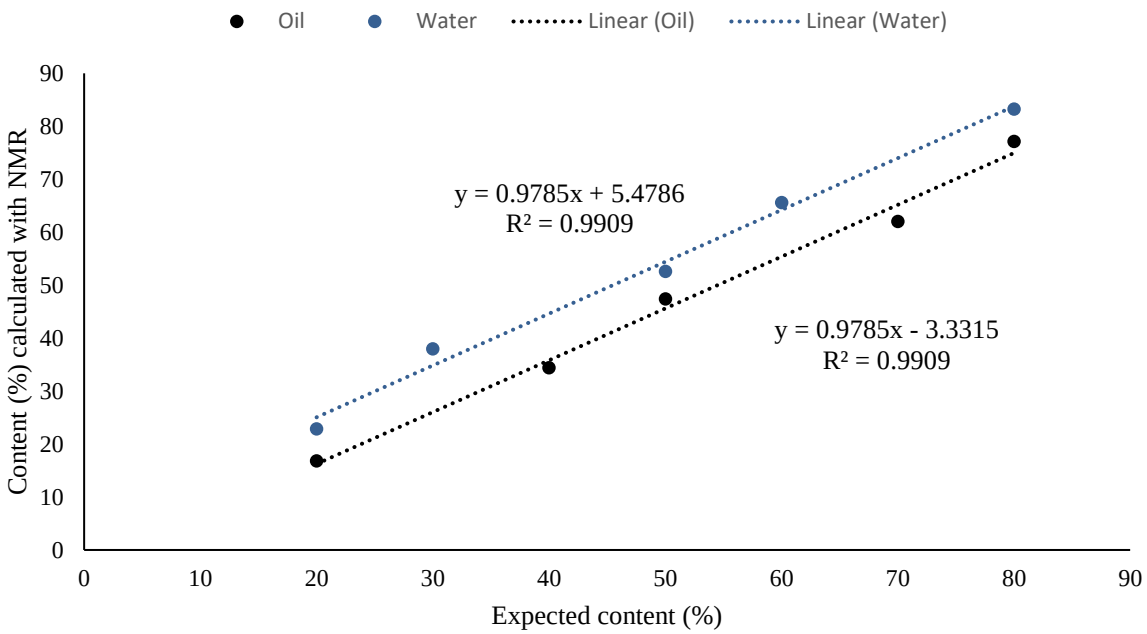

Figure 3.9. Relationship between the oil and water contents (%) calculated with NMR and the expected contents (%).

CPMG T_2 relaxation times curves for all oil-water mixture standards are shown on Figure 3.10. As the oil relaxes faster than the water (LaTorraca *et al.*, 1998), the standard with more oil (80%) had a more rapid decay compared with the other standards with less oil and more water content.

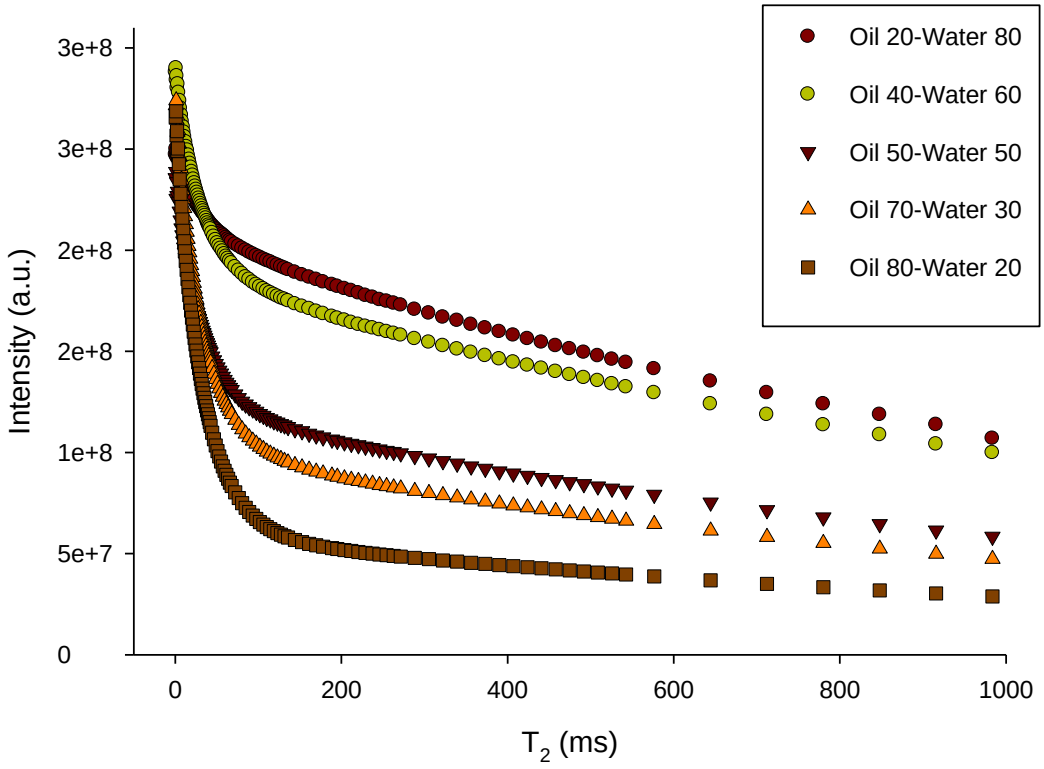

Figure 3.10. CPMG T_2 relaxation times for high-field NMR runs of oil and water mixtures standards.

For further confirmation of the reliability of the NMR data, the percentage difference between the 1D proton spectra and T_2 decay data at each oil and water mixture standard is shown in Table 3.6. Most of the percentage difference values were less than the accepted 5% (R. M. Kowalczyk (2015), pers.comm., 20 March), indicating agreement in the 1D proton spectra and T_2 decay data and supporting the reliability of the results.

Table 3.6. Percentage differences between the 1D proton spectra and T_2 decay data of the oil and water standards.

Standard Oil+Water (%)	Oil (%)			Water (%)		
	1D proton spectra	T_2 decay	Difference (%)	1D proton spectra	T_2 decay	Difference (%)
1: 20 + 80	14	17	19	86	83	3
2: 40 + 60	33	34	3	67	66	1
3: 50 + 50	53	47	12	47	53	12
4: 70 + 30	61	62	2	39	38	2
5: 80 + 20	77	77	0	23	23	0

Once the method was checked, the oil and water contents were calculated in the oil sludges. Oil and water contents obtained with NMR are shown in Table 3.7.

Table 3.7. Oil and water contents in the oil sludges determined by nuclear magnetic resonance (NMR).

Sample	Oil (%)	Water (%)
WSS	81 (±6)	19 (±6)
ODS	1 (±0.26)	99 (±0.26)
STS	50 (±14)	50 (±14)
RS	39 (±1)	61 (±1)
NSC	88 (± 11)	12 (±11)

* The mean of the percentage values with the standard deviation (in parentheses) are shown (n = 3).

The same trends of the proportions from the oven drying method of both water and oil contents were still found in the NMR data. However, contrary to the oven drying method, the water content of the NSC sludge found with NMR was the lowest. This value confirmed that the water content was overestimated by the drying method with a five-fold increase from the value obtained by NMR. Consequently, the oil content was the highest (88% ± 11), as

confirmed with the highest amount of organic material for this sludge obtained from the oven-drying method. Similarly, the lowest organic material found in ODS was confirmed with the low amount of oil by the NMR. WSS had a higher amount of oil than ODS, STS, and RS.

All oil sludges samples had two components (oil and water) detected on the CPMG T_2 decay data similar to the oil and water mixture standards. However, the NSC sludge had a third extra component. This component was not included in the analysis of this sample, for the sake of assessing only the water and oil contents. However, further analysis has to be done to evaluate how to treat this additional component by fitting it to the T_2 exponential decay equation.

The T_2 relaxation time curves for all sludges are shown in Figure 3.11. Since both WSS and NSC sludges had higher contents of oil, the curves showed a rapid decay due to the faster relaxation of the oil component. Conversely, ODS had a slower decay due to the higher water content.

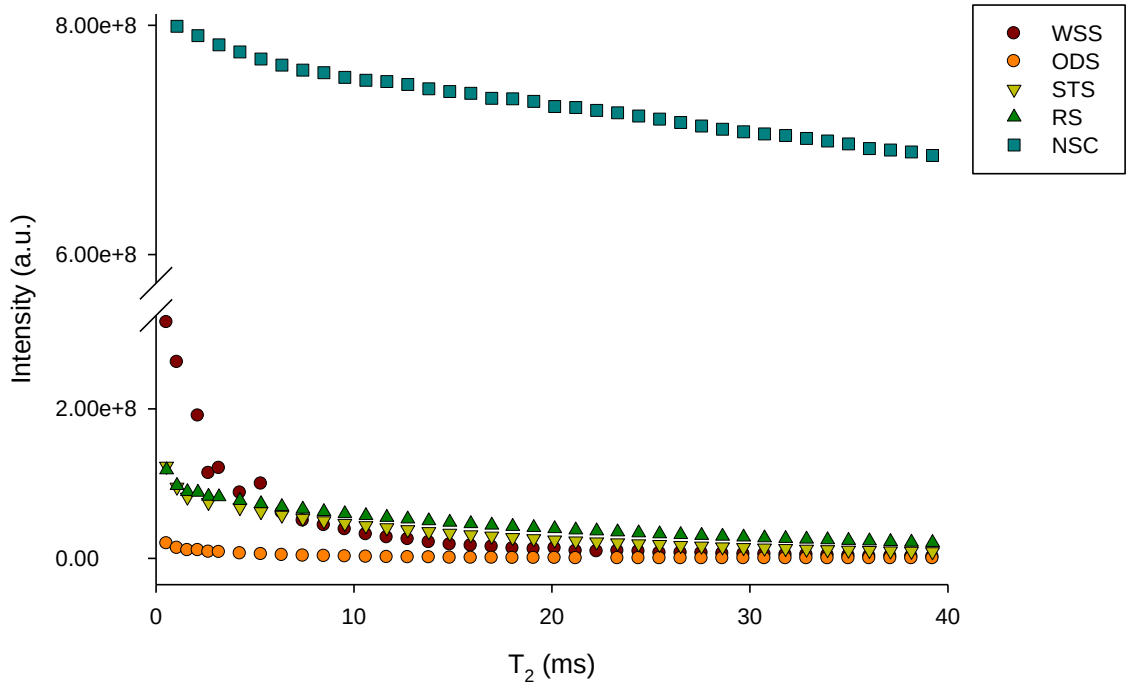

Figure 3.11. T_2 relaxation curves (CPMG) of high-field NMR runs of all oil sludge samples (WSS, ODS, STS, RS, NSC).

3.3.2.4. EPH analysis of oil sludge

Figure 3.12 shows the mean values of each EPH fraction for all the sludges. A two-way ANOVA showed that there was a highly significant effect of the type of sludge ($p < 0.01$) and the hydrocarbon fractions factor ($p < 0.01$). Therefore, each sludge was unique as expected. Consequently, the interaction between both factors was highly significant ($p < 0.01$). The total EPH fractions for all sludges were 33,000 (±3,000) ppm for WSS, 6,000 (±145) ppm for ODS, 1,550 (±506) ppm for STS, 949 (±392) ppm for RS, and NSC had a total EPH concentration of 68,000 (±6,070) ppm. ODS, NSC, WSS had a high percentage of the C_{10}-C_{18} aliphatic fraction with 98, 70, and 60%, respectively. On the other hand, STS had 13%, and RS had 10% of this fraction. The percentage of the C_{19}-C_{36} aliphatic fraction was higher for STS and RS (83 and 85%, respectively) compared to ODS (0.53%), WSS (33%) and NSC (30%). All the sludges had a low percentage of the C_{11}-C_{22} aromatic fractions within a range of 1% to 8%.

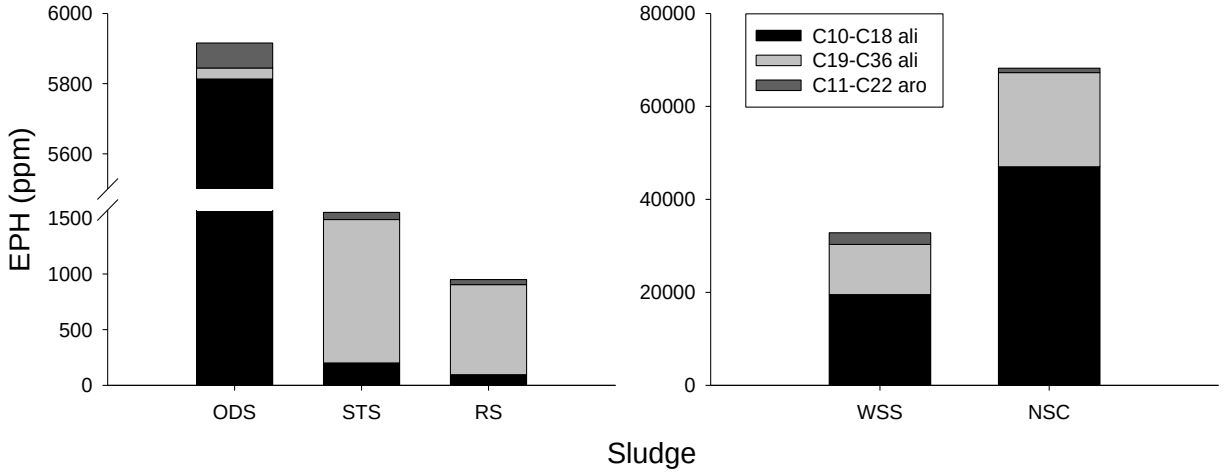

Figure 3.12. Extractable petroleum hydrocarbons (EPH) mean values for the three fractions (C_{10}-C_{18} and C_{19}-C_{36} aliphatics and C_{11}-C_{22} aromatics) of all sludges.

The chromatograms of the EPH aliphatic fractions for all the five sludges are shown in Figure 3.13. Since the WSS sludge was the first sludge to be analysed, the GC method applied at that time had a running time of 26.50 minutes. For the other four sludges, the running time was 36.50 minutes because another method was used. As mentioned in section 3.2.2.6, the GC method was changed to determine the PHCs concentrations in terms of EPHs because the volatile fraction (VPHs) included in the TPH group could not be determined in the GC-FID machine with the previous method applied for the WSS sludge. The inability to determine these VPHs could be due to the easy volatilisation of these compounds that reduce the concentrations in the samples, and these could be below the detection limit of the GC-FID used in this study (0.5 $mg \cdot l^{-1}$). The GC profiles of WSS, STS, and RS had unresolved complex mixtures (UCM) after the C_{20} peak. In fact, these humps contributed with a higher concentration of the C_{19}-C_{36} aliphatic fraction in STS and RS (Figure 3.12, Figure 3.13C and D). The UCMs are a group of several overlapped compounds that cannot be resolved by GC-FID (Frysinger *et al.*, 2003). These humps are often observed in degraded crude oils (Gough and Rowland, 1990; Peters *et al.*, 2005). UCMs are observed in lubricating oils and other refined oil fractions (Gough and Rowland, 1990). In facts, RS and STS sludges had waste engine oil with oil additives to enhance the lubrication feature of the oil.

The GC profile of NSC (Figure 3.13E) was similar to the profile of a conventional pure crude oil (Figure 2.3A).

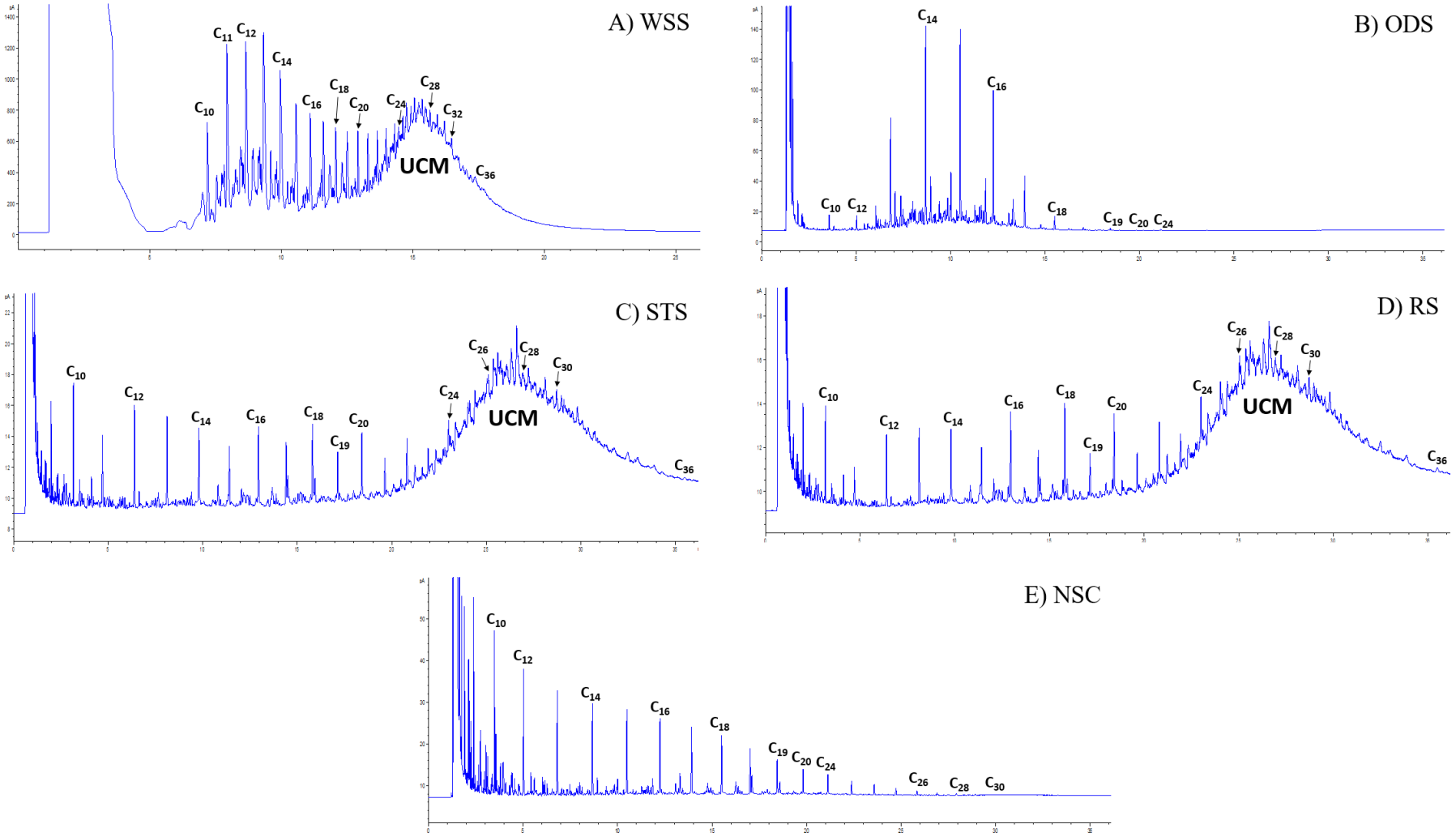

Figure 3.13. Gas chromatograms of the EPH aliphatic compounds for all the analysed oil sludges. The retention times (min) are shown on the x-axis. The signal magnitude of the peaks was pA (picoamps; y-axis). The unresolved complex mixtures (UCM) are indicated. The total running time of GC runs for B) to E) was 36.5 minutes and for A) was 26.5 minutes.

3.4. Discussion

3.4.1. Micelle sizes of the surfactants

DLS has been reported to be used in the measurement of the CMC (Malvern, 2006b; Rosen and Kunjappu, 2012; Topel *et al.*, 2013). However, in this study, it was not possible to use this method to determine CMC, since the background noise from the solution was increasing the polydispersity index (PDI). The high polydispersity at the CMC point hampered the detection of micelles because the background noise (e.g. dust particles) was higher than the number of micelles. The reason is related to the fact that at the CMC not all of the surfactants monomers are grouped into micelles; only 50% of the surfactant are micelles and the remaining 50% are surfactant monomers (BeckmanCoulter, 2013). Therefore, the monodispersity degree of the micelles at CMC was not high enough to ensure a proper measurement of the hydrodynamic diameter, so micelles were detected at higher concentrations than CMC with the DLS. To illustrate, the SDS micelles could only be detected at almost two-fold the CMC, while T80 had reliable results at three-fold the CMC. Another limitation was related to the micelle shape because apart from the common spherical shape, the micelle can be spherical and cylindrical. In addition, RL monomers can agglomerate as irregular and spherical vesicles and lamellae (Pornsunthorntawee *et al.*, 2009). Figure 3.14 shows the different types of agglomerations that RL can adopt.

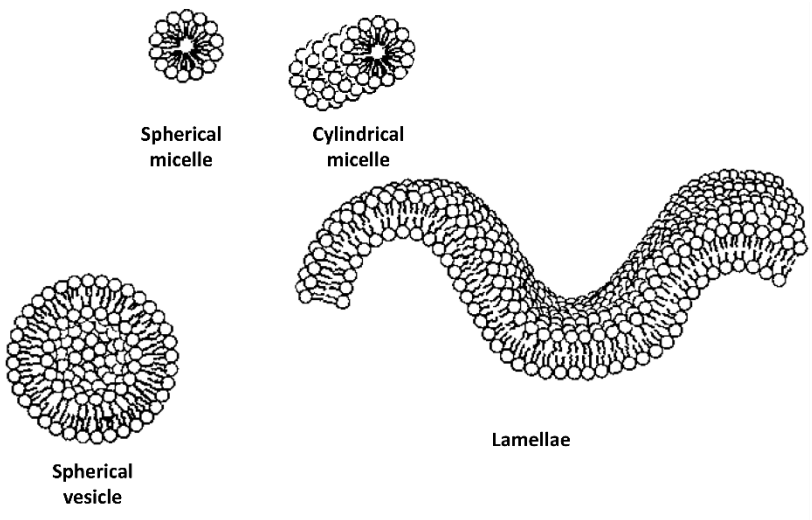

Figure 3.14. Types of agglomerations of RL. Adapted from Champion et al. (1995).

Viscosity and micellar size are directly related in non-ionic surfactants (Fanun, 2008). The viscosity for the non-ionic surfactants used was 375-480 cP (Sigma-Aldrich) for T80, 240 cP for TX100 and 260 cP for TX114 (MP Biomedicals). Results from Table 3.2 showed that micelle size of TX100 was the smallest (7.62 ± 0.05 nm) compared to T80 (12.1 ± 0.17 nm) and TX114 (14.58 ± 0.006 nm). For instance, the highest viscosity can be related to the greatest micelle size in the case of T80; as Tadros (2005b) has mentioned for longer chain surfactants (e.g. T80, C_{64}) in which micelles grows as the viscosity increases. This author also said that there is a proportional increase in the viscosity in a non-ionic surfactant solution as the concentration increases. At the CMC point, the degree of viscosity rises rapidly, and the solution starts to have a gel-like appearance as the concentration increases due to the hexagonal type liquid crystalline structure generated (Tadros, 2005a). At these high viscosities, it is recommended to ensure a homogeneous mixing of the surfactant in solution by vigorous mechanical shaking (Prieto and Calvo, 2013).

According to the results obtained, DLS can be only used for detecting and estimating the size of the micelles at concentrations higher than the CMC. For these reasons, the pendant drop method was selected for determining the CMC values of the surfactants.

3.4.2. CMC and surface activity

The CMC range is stable and narrow; it depends on the experimental conditions used in the different studies. For instance, variations in concentration of surfactant can affect the size, shape, and structure (from spherical to lamellar micelles) (Dominguez *et al.*, 1997; Rosen and Kunjappu, 2012). For instance, the micelle size of RL variated from 4CMC and 7CMC (Table 3.2).

The non-ionic surfactants used (TX100, TX114, T80, and RL) had lower CMCs compared to the anionic surfactant (SDS). In general, when both non-ionic and anionic surfactants have the same alkyl chain length, the CMC is two orders of magnitude lower for non-ionic surfactants compared to its corresponding anionic (Tadros, 2005a). Also, the aggregation number for the non-ionic surfactants is higher, and their micelle sizes are bigger compared to their ionic surfactant counterparts (Attwood and Florence, 2012). Therefore, bigger micelles can solubilise more oil inside their hydrophobic core (Rosen and Kunjappu, 2012).

Patist et al. (2000) mentioned that usually, in the case of non-ionic surfactants such as T80, expected abrupt changes in the surfactant concentration and surface tension curve can fluctuate due to high molecular weights (T80 = 1309.68 $g \cdot mol^{-1}$) and impurities in the surfactant affecting the CMC values. Indeed, T80 had a CMC 100-fold times greater (1.12 mM) compared to the most common reported CMC value in the literature (0.012 mM). However, Peng et al. (2011) reported a 10-fold higher value for CMC (0.119 mM). Nevertheless, the CMC values obtained for T80 can be used because the CMC value was determined at the point where the surface tension remained stable after a decline; which is the formal definition of CMC. Therefore, the CMC result for T80 is comparable with the other surfactants used, because all were defined in terms of the experimental CMC obtained in this study following the same procedure (i.e. dilution from a 10% surfactant stock and CMC determination by the pendant drop method). After the CMC was analysed, the surface activities of all surfactants were measured below, at, and above the CMC.

T80 has a viscosity of 375-480 cP (Sigma-Aldrich), and this was the surfactant with the highest viscosity in this study. The surfactants were added using a micropipette due to the considerable low concentrations to reach the CMC at the millimolar level. Since the surfactants were viscous, the micropipette tip was cut to have a wider diameter at the tip. This cutting was

done for all of the surfactants when making the stock solutions, except for SDS and RL. The former was measured by weight as the SDS was available as a powder. RL was diluted when it was acquired from the supplier, so the viscosity was low in the solution. Even though the cutting of the micropipette tip improved the suction of the surfactants and it was not observed any surfactant remnants in the tip, it is very likely that some surfactant remained on the walls of the tip. Therefore, it is recommended to prepare the surfactant stock solution by weight using a 4-digit analytical balance for precision as the density for T80 is known (1.064 $g \cdot cm^{-3}$).

One common indicator of the surfactant effectiveness is the maximum reduction that a surfactant can achieve on the surface or interfacial tension (Schramm, 2000a). RL, TX114, and TX100 (lower CMCs) had higher surface activities than SDS and T80 (higher CMCs) as it could be evidenced in the oil displacement test. In fact, Rosen and Kunjappu (2012) mentioned that the surfactant effectiveness is greater when the surfactant has low surface tensions at the CMC point (Figure 3.6).

3.4.3. Physicochemical analyses of oil sludges

ODS had the highest dry matter content due to the large presence of sediments as this was an oil drilling sludge, and NSC had the highest dried organic material due to the high presence of hydrocarbons. Also, NSC had the highest water content according to the oven-drying method. However, since NSC is mostly crude oil, it was expected that a lower amount of water would be in this sludge. In fact, the NSC sample was mostly crude oil after drying at 105°C as shown in the picture from Table A 1 from Appendix A. It could be possible that after heating at 105°C, all this weight was lost due to volatilisation of the light hydrocarbons. In fact, the C_{10}-C_{18} aliphatic fraction showed a higher concentration than the C_{19}-C_{36} aliphatic fraction (Figure 3.12 and Figure 3.13). Also, Jin et al. (2014) found that the oven drying method for water determination was overestimated due to volatilisation compared to other methods such as NMR, Karl-Fischer titration, and the azeotropic distillation by the Dean-Stark method. Therefore, the NMR method was used to confirm the oil and water content in the sludges and to test if the oven dried method was overestimating the water content of all samples.

Low-field NMR has been used before as a promising technique for the rapid measurement of the oil and water content of oil sludges (Jin *et al.*, 2013). Before analysing the

sludges, a series of oil/water standard mixtures were measured in the NMR to check the method. There was an agreement in the majority of the percentages because the relative errors between the expected and obtained values were less than 15% (Sivarao *et al.*, 2014). Although there were discrepancies between the expected and experimental oil/water ratios on two samples, there was a good correlation in both expected and experimental values in the other ratios. Furthermore, the 1D proton spectra and T_2 decay data at each oil and water mixture had percentage differences less than the accepted 5% for most of the samples.

In this chapter, high-field NMR was used to analyse the oil sludge, and it looked promising as well as it was reported before for the low-field NMR. In fact, it was found that the water and oil (organic material in the drying method) were similar in both the oven-drying and NMR methods. Although it was not possible to calculate the correct position of the oil and water peaks in the 1D spectra due to the paramagnetic impurities and emulsions from the oil sludge, the CPMG T_2 decay data showed differences among the sludges which allowed to calculate the oil and water contents.

Besides the expected two components for oil and water, the NSC samples had one unexpected third component in the CPMG T_2 decay data. Therefore, it is necessary to re-analyse these data and add this third component in the T_2 decay equation to see if there is any improvement in the exponential fit. This problem is caused by the difficulty to get a precise 90° pulsation. For instance, the paramagnetic and salt contents present in the sample can contribute to this variation in the precision of the 90° pulses (Simpson *et al.*, 2011). The goal of the pulse sequences is to excite the signals present in the sample, so these signals can be detected by the NMR spectrometer (Derome, 1987). Despite this drawback with the NSC sample, these data are reliable to confirm the proportion of oil and water in the oil sludges due to the validation of the method performed with the oil and water mixtures.

Sørland et al. (2004) mentioned that oil and water peaks are sometimes difficult to resolve due to their similar T_2 transverse relaxation times to the magnetisation signals, and Jin et al. (2013) suggested that the addition of paramagnetic ions such as $MnCl_2{\cdot}4H_2O$ allowed the separation of the oil and water peaks. However, it was not necessary to add the paramagnetic ions in the NMR experiment done for this chapter, since both signals were clearly resolved and separated in the oil sludges. Probably, this situation is due to the original presence of metals in the samples (Table 3.4).

The trace elements analysed for the oil sludges showed lower concentrations compared to the reported values for oil sludges, except for the WSS sludge. All sludges had high Ca, Fe, Ni and Zn concentrations. In fact, Schirmacher et al. (1993) found that higher concentrations of Ca, Fe, and Zn are characteristic of oil sludges in their study of 29 sludges samples (Schirmacher *et al.*, 1993).

NSC had the highest total EPH concentration (68,000 ppm) as expected due to its higher amount of crude oil. The other sludges had concentrations less than 6,000 ppm. It was anticipated that ODS had the lowest concentrations since it had the lowest oil and organic material contents. The information obtained from the EPH analysis is a starting point to know the potential use of the oil from the sludge as oil refinery feedstocks. The use as fuel depends on the presence of light or heavy aliphatic fractions, so a high percentage of C_8-C_{24} aliphatics is a potential source of diesel (Giles, 2010). WSS, ODS and NSC had a high percentage of the C_{10}-C_{18} aliphatic fractions, whereas STS and RS had high percentages of the C_{19}-C_{36} aliphatic fractions. The aromatic fractions had the lowest proportions in all sludges. In fact, the proportion of aliphatic compounds in the oil sludges is generally higher compared with the aromatics (Ward *et al.*, 2003).

WSS, STS, and RS sludges had the presence of unresolved complex mixture (UCM) peaks in the chromatogram. As mentioned before, UCMs are characteristic of crude oils at different stages of degradation; the humps are higher at advanced stages of degradation (Peters *et al.*, 2005). Giles (2010) mentioned that biodegradation events by the native and crude oil-resistant microbiota can occur in the storage tanks (where oil sludge can be found) as the water and sediments found in the bottom can promote this biodegradation. Although the oil sludges were collected freshly from their sources, there is a possibility of some weathering and degradation events in these sludges as these samples were stored in tanks (Giles, 2010).

3.5. Conclusions

In contrast to earlier findings (Malvern, 2006b; Rosen and Kunjappu, 2012; Topel *et al.*, 2013), it was found that DLS was not a reliable or precise method to determine the CMC of a surfactant. The detection of the exact CMC was hampered due to the high polydispersity in the sample below and even at the CMC. The sample was only acceptable for analysis at much higher concentrations than CMC where the solution had a homogenous amount of micelles. Therefore, DLS was only used to confirm and determine the size of the micelles, whereas the pendant drop method was used to determine the CMC.

Even though the CMC values were different among the surfactants, the concentrations used in the oil sludge washing experiments can be defined in terms of this concentration for all the different surfactants. The pendant drop method was consistent with the results obtained in the literature, except for T80; its CMC was 100-fold higher. This result has not been reported before, and certainly, it was not possible to determine the reasons in this study. Despite this situation, the experimental CMC value obtained for T80 was used, as it was determined at the same conditions of the other surfactants. Also, it followed the same principle of the determination of the CMC because the surface tension had an abrupt decrease and stabilisation for all the surfactants analysed. This event indicates the presence of micelles at the CMC. Also, the reduction of surface tension of the water in T80 was similar to the data reported previously.

RL, TX100, and TX114 had the highest areas of the clear halo zones. These results indicated that these surfactants had a high surface activity compared to T80 and SDS. Indeed, it can be expected that these surfactants will have a significant performance in the oil recovery experiments of this thesis.

The oil sludges analysed had different amounts of oil, water, and sediments as they came from different sources. This fact is important because it can validate the oil sludge washing method studied in this thesis using a variety of oil sludges. The oven-drying method is not reliable for sludges with a higher amount of the light hydrocarbon fraction (C_{10}-C_{18}). For example, the water content of NSC was overestimated because this sludge contained the highest amount of this fraction that could be evaporated when the water content was determined. In fact, NMR confirmed that NSC had the lowest water content as this sludge was mostly crude oil.

High-field NMR seems promising to determine oil and water contents in the sludge because it was validated by the analysis of oil and water standard mixtures. The results from NMR were able to replace the data of the oven-drying method. The high-field NMR method shows promising results, and it should now be rigorously tested.

The oil sludges had high levels of Ca and Fe which are characteristic of these materials (Schirmacher *et al.*, 1993). However they had concentrations of other PTEs within the accepted limits for the agricultural use of sludges as amendments. Only the WSS sludge had higher values, specifically for Cr, Cu and Ni. Also, when the oil from the sludge is reused, the trace elements data can anticipate any issues due to the presence of unwanted elements, such as Na and Ni, which are corrosive. Moreover, potential toxicity issues due to these elements can be predicted.

As it was mentioned before, each sludge was unique, and it was confirmed by the analysis of the total EPH concentrations analysis. WSS, ODS and NSC was rich in C_{10}-C_{18} aliphatic fractions. On the contrary, STS and RS had high percentages of the C_{19}-C_{36} aliphatic fractions. Indeed, this information is relevant as it can be known in advance the potential use of the recovered oil as a fuel depending on the concentrations of each fraction. Also, the state of weathering and degradation of the oil in the sludge can be checked with the presence of UCMs in the gas chromatograms, as it was observed for WSS, STS, and RS.

Finally, now that all of the oil sludges and the surfactants were characterised, the oil sludge washing method can be tested.

Chapter 4 - Oil sludge washing using surfactants from an oil-water separator sludge, a preliminary study

4.1. Introduction

This chapter described the first oil sludge washing (OSW) study of this thesis performed with the WSS sample (Chapter 3. Section 3.3.2.1) from an oil-water separator. Oil-water separators are based on gravity to treat wastewater from oil refineries. Figure 4.1 shows a schematic diagram of an oil-water separator. The sediments and water are separated by gravitational force, and the oil is recovered on the top. A floating oil skimmer is used to remove the oil. The baffles distributed along the separator device help to keep the sediments, water, and oil separated. The separated water goes through an outlet for further treatment if needed. A common problem with oil-water separators is the generation of sludge due to the accumulation of settled solids from the wastewater at the bottom of the separator (See the bottom-right region in Figure 4.1). Some oil remnants can be adsorbed or absorbed strongly into the settled solid particles from the oily wastewater. In fact, this is the origin of the oil sludge used in this study.

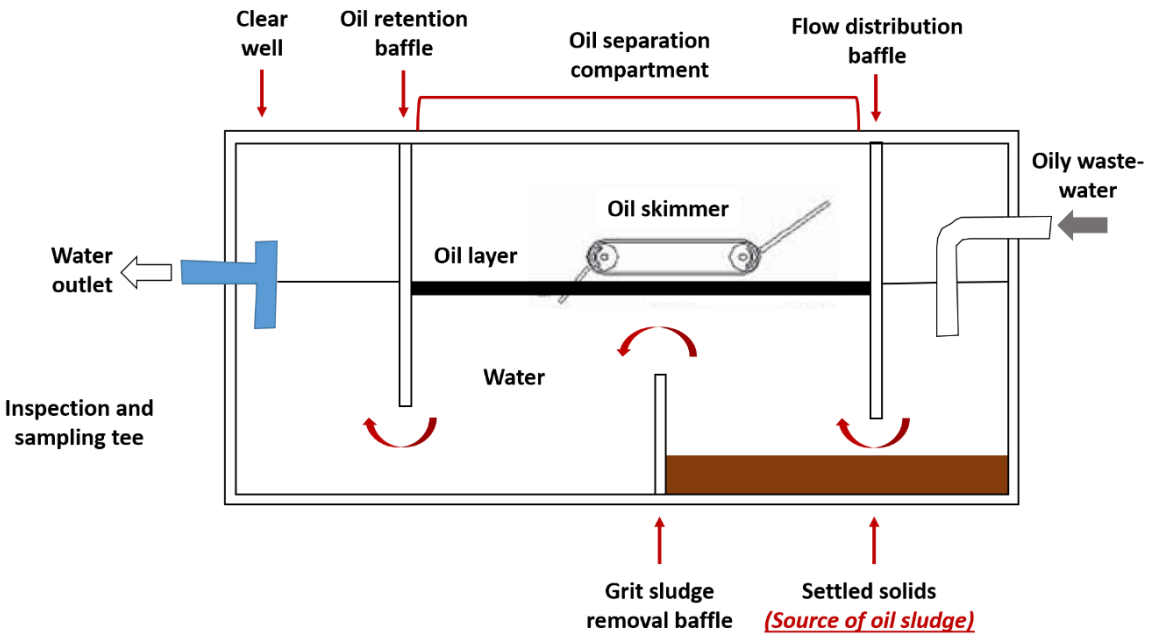

Figure 4.1. Diagram of a gravity oil-water separator. Based on Romano (1990) and Kajitvichyanukul et al. (2006).

Oil sludge washing (OSW) is a process derived from similar procedures with soil, which use liquid solutions to remove contaminants from soil (Pacwa-Płociniczak *et al.*, 2011). Surfactants are used in the washing to reduce the interfacial tension of W/O macroemulsion of the sludge, and the agitation performed in the washing process leads to the breakdown of the emulsion (Rosen and Kunjappu, 2012). Before an OSW protocol is performed, it is necessary to assess the surfactant characteristics such as critical micelle concentration (CMC), surface activity and micelle size of surfactants. These characteristics are important because they are related to the performance of surfactants in the oil recovery. Therefore, the surfactant characteristics were analysed on Chapter 3. Schramm and Marangoni (2000) stated that the determination of CMC is crucial in the petroleum industry because concentrations higher than the CMC favour the enhanced oil recovery. In this case, the presence of micelles can decrease the interfacial tension between the oil and water, and therefore it can can enhance the solubilisation of oil into the micelles. Moreover, other compounds known as co-solvents are used in the OSW.

Co-solvents can be added with surfactants to aid in the extraction of oil; these compounds are non-surface active that enhance the effectiveness of the surfactant (Schramm, 2000b). The combination of surfactants and co-solvent modifies the properties of the interfacial film leading to a coalescence and separation of the emulsion (Sjöblom *et al.*, 1990). Co-solvents such as toluene were used by El Naggar et al. (2010) and Atta and Elsaeed (2011) to extract oil. OSW has been implemented in the treatment of oil sludges. However, there has been no detailed investigation of the influence of the surfactant type, concentration and application ratio in the washing of oil sludges, especially in different types of oil sludges.

Since this is a preliminary study, the three factors evaluated (i.e. surfactant type, surfactant concentration and surfactant to oil sludge (S/OS) ratio) had five levels each to have a broad overview of the factors. If a full factorial design is applied, a total of 125 experimental runs ($5 \times 5 \times 5$, the number of levels per each of the three factors) are obtained and 375 runs in triplicate. Therefore, this case has a considerable high amount of experimental runs, and alternative experimental designs should be used. However, fractional factorial designs such as Plackett-Burman cannot be used because these designs only work for two-level factors. Moreover, a response surface design is not suitable because all the factors have to be numeric, and the surfactant type is a categorical factor. After searching for an appropriate experimental design, the Taguchi experimental design was considered. This experimental design method is used, especially in food and engineering industry, to find the optimal levels of determined

parameters using a minimum number of experimental runs at an early experimental stage. Moreover, the Taguchi experimental design evaluates how factors or parameters are affecting the performance of a response variable (Fraley *et al.*, 2007). The primary objective of this design is to generate a product with high quality and standard at low costs, and it can also be used to optimise a process (Fraley *et al.*, 2007). The method is a combination of experimental design and analysis which is based on classical methodologies such as orthogonal arrays and other non-classical types of methods such as signal-to-noise (S/N) ratios (Charteris, 1992). An orthogonal array is defined as a matrix of *"n"* number of rows and columns in which the columns correspond to a selected factor and the rows have the defined levels or states of each factor (Fraley *et al.*, 2007). The orthogonal array notation is L_a (b^c), where *a* is the number of experimental trials, *b* is the number of levels, and *c* is the number of factors (Fraley *et al.*, 2007). Also, Genichi Taguchi, the engineer and statistician who developed the method, considered that the main reason to use an orthogonal array is its ability to detect interactions among the factors (Antony, 2002). The advantage of using this type of array is that the Taguchi method can test pairs of combinations (Figure 4.2) instead of testing all the combinations (e.g. factorial design) (Fraley *et al.*, 2007). To summarise, the method will collect all the necessary data to assess the factor or factors that had large effects on the response variable without extensive experimentation (Fraley *et al.*, 2007). By doing this, the factors and levels can be ranked to find the combination that can optimise the response variable.

Experimental Run	Factor 1	Factor 2	Factor 3	Factor 4
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Figure 4.2. L_9 Taguchi orthogonal array with four factors and three levels. The arrows show the interaction between the pairs of combinations that the Taguchi method analyses (Fraley *et al.*, 2007).

The Taguchi design can be used for static and dynamic response experiments. For the former, the response variable has a fixed level and no input signal before the experiment. On the contrary, the dynamic response experiment has an input signal on the response variable (Minitab, 2000). A Taguchi experimental design can be done in experiments from 3 to 50 factors.

The outputs from the Taguchi experimental design are response tables for S/N ratios, mean and standard deviation. These tables are essential for the ranking of the factor and levels, so it can be determined which factors maximise or minimise the response variable. This ranking is relevant to determine which factor has the largest effect on the response variable. Briefly, the Taguchi orthogonal array analyses the response variable results using the signal-to-noise (S/N) ratio, which is a statistical index of performance of the response variable. The S/N ratio consists in the logarithmic ($\log_{10}$) of the mean (signal, S, result) to the standard deviation (noise, N) of the result (Bhinder *et al.,* 2015). There are three types of S/N ratios which can be adjusted depending on the objective of the study. These three types include the maximisation, minimisation or targeting of a specific value of the response (Fraley *et al.,* 2007; Bhinder *et al.,* 2015). Taguchi methods are applied at early stages of the experimental development (Fraley *et al.,* 2007), so it can be considered in this experimental design. Future experiments can be designed based on the Taguchi results, once the parameters with the higher effects are found.

Recently, Zheng et al. (2012) have used the Taguchi method in an oil recovery from oil sludge study using biosurfactants. The factors used were biosurfactant type and concentration, pH, salinity and co-solvent with four levels each [L_{16} (4^5)]. Similarly, Yan et al. (2012) applied the Taguchi method in a study of oil recovery from refinery oily sludge using rhamnolipids. The factors used were carbon to nitrogen (C/N) ratio, temperature, sludge-water ratio, and inoculum size of the rhamnolipid-producing bacteria (*Pseudomonas aeruginosa*) with three levels of each factor [L_9 (3^4)] (Yan *et al.*, 2012).

Due to the importance of surfactants in the OSW, there is a need for testing specifically different types of surfactants and their influence of their concentrations and surfactant to oil sludge (S/OS) ratios in the oil recovery from oil sludges. To date, these parameters have all been studied in oil drill cuttings washing studies (Yan *et al.,* 2011) and multiple soil washing studies (Deshpande *et al.,* 1999; Urum *et al.,* 2003; Urum and Pekdemir, 2004; Urum *et al.,* 2006; Pornsunthorntawee *et al.,* 2008; Peng *et al.,* 2011; Zhang *et al.,* 2011a). The most studied

oil sludges are produced in the bottom of oil storage tanks (Rahman *et al.*, 2003; Hu *et al.*, 2013). However, to our knowledge, no previous OSW study has investigated specifically the interaction of surfactant type, surfactant concentration and S/OS ratio in the oil recovery from oil-water separator sludges. The surfactants used in the pilot study presented in this chapter are Triton X-100 (TX100), sodium dodecyl sulphate (SDS), Tween 80 (T80), rhamnolipid (RL), and Triton X-114 (TX114).

The aim of this study was to analyse the interaction of the surfactant type, concentration and application ratio to oil sludge (S/OS) for the maximisation of the oil recovery rate (ORR %) in an oil sludge washing (OSW) process from an oil-water separator sludge (WSS).

4.2. Materials and Methods

4.2.1. Oil sludge

Oil sludge (WSS as named in Chapter 2) was sampled in England. This oil sludge came from an oil/water separator in an oil refinery. The total extractable petroleum hydrocarbons (EPH) concentration was 33,000 (±3,000) ppm. The sludge was viscous and black. It has a semi-solid cake state at room temperature. For more physicochemical characteristics, see Chapter 3 (Section 3.3.2).

4.2.2. Surfactants

90% pure rhamnolipid with 5% liquid (RL) was obtained from AGAE Technologies (Corvallis, Oregon, USA). SDS was supplied by BDH Laboratory supplies. T80, TX114 and TX100 were laboratory grade and supplied by Sigma-Aldrich. All concentrations needed for the study were prepared from an intermediate stock solution of 10% (w/v) of SDS and RL, and 10% (v/v) of TX100, T80 and TX114 dissolved in ultrapure water (18.2 MΩ·cm).

4.2.3. Oil sludge washing (OSW) protocol

Absolute surfactant concentrations were expressed in terms of critical micelle concentrations (xCMC) due to the wide inter-surfactant variation of CMC (Deshpande *et al.*, 1999). For instance, CMC values for anionic surfactants can range from 10^{-3} – 10^{-2} M and for non-ionic surfactants from 10^{-5} – 10^{-4} M (Schramm and Marangoni, 2000). The CMC values were calculated in Chapter 3 (Section 3.3.1.2). To recall, the calculated CMC values were 0.048 mM (RL), 0.28 mM (TX100), 0.36 mM (TX114), 1.12 mM (T80), and 8.37 mM (T80).

The determined S/OS ratio (Yan *et al.*, 2011; Zheng *et al.*, 2012) and surfactant concentration were added to a vial at room temperature. Toluene was added to the mixture in a 1:1 to oil sludge ratio basis (co-solvent to oil sludge, C/OS). This solvent is commonly used in the extraction of oil hydrocarbons. For instance, El Naggar et al. (2010) reported that toluene was the best solvent to recover hydrocarbons from sludge (76%) compared to the other solvents evaluated such as *n*-heptane, methylene and ethylene dichloride, diethyl ether, and naphtha and kerosene cut. Also, toluene was used as a carrier of different solutions of non-ionic biosurfactants to treat oil sludge (Atta and Elsaeed, 2011). Jennings Jr and Abou-Sayed (1994) used toluene in their studies to reduce the viscosity of crude oil, and it was an efficient oil extractant from heat-treated oil shales due to its recovery rates of 90% (Bock *et al.*, 1984). The vials were placed laterally on an orbital shaker for 1 hour at 250 rpm. Then, the samples were left to settle overnight for 12 hours to ensure complete separation and sedimentation (Urum *et al.*, 2004). Three phases were evidenced: a top layer of oil and toluene, a middle layer of water and surfactant, and the bottom layer of sediments. Vials were frozen at -25ºC for 12 h (Zhang *et al.*, 2012) and thawed at room temperature to enhance and aid in the recovery of the unfrozen oil top layer with toluene as described in Section 2.11 and Figure 2.8. This top layer was taken, and the toluene was evaporated under a gentle nitrogen stream. The recovered oil was measured by weight. Oil recovery rate (ORR) % (Zubaidy and Abouelnasr, 2010; Hu *et al.*, 2015) was calculated with the mass of recovered oil (Equation 4.1).

$$ORR = \left(\frac{Mass\ of\ recovered\ oil}{Mass\ of\ oil\ sludge}\right) \times 100\%$$

Equation 4.1. Oil recovery rate.

4.2.4. Experimental design for maximisation of oil recovery

To establish the optimal surfactant concentration and S/OS ratio for the five type of surfactants and concentrations, the factorial design with three factors (columns) and five levels (rows) is shown in Table 4.1. The measured or response variable was the oil recovery rate (ORR %).

Table 4.1. Factors and levels of the experimental design for the optimisation OSW parameters.

Level	Surfactant	Concentration (xCMC)[a]	S/OS ratio[b]
1	TX100	0.5	1:1
2	SDS	1	2:1
3	T80	2	3:1
4	RL	4	4:1
5	TX114	5	5:1

[a] Concentrations were selected according to Zhang et al. (2011a) and Pornsunthorntawee et al. (2008).
[b] S/OS ratio: surfactant to oil sludge ratio. Ratios were determined according to Yan et al. (2011).

Since the experimental design of this study had a possible number of combinations of 125 (375 in triplicate) with three factors or parameters and five levels (5^3) (Table 4.1), a Taguchi orthogonal study was considered. This type of experimental design can be implemented mostly in early stages to know the effect of the factors involved (Fraley *et al.*, 2007).

According to the orthogonal array selector, the number of sets or experiments for three factors and five levels is 25, L_{25} (5^3). This design was repeated five times. At this point it has to be mentioned that these are not technical replicates; these are blocks or repetitions of the Taguchi design. The blocking is considered to be a categorical variable to account for variation of the ORR that is not caused by the factors. By doing this, the impact of uncontrolled variations can be reduced (Minitab, 2014). In this study, each block (Taguchi design) was done per day. Table 4.2 shows all combinations (25) analysed in the Taguchi design.

Table 4.2. L_{25} (5^3) orthogonal array with the experimental runs used in each block.

Run	Surfactant type	Surfactant concentration	S/OS ratio*
1	TX100	0.5CMC	1:1
2	TX100	1CMC	2:1
3	TX100	2CMC	3:1
4	TX100	4CMC	4:1
5	TX100	5CMC	5:1
6	SDS	0.5CMC	2:1
7	SDS	1CMC	3:1
8	SDS	2CMC	4:1
9	SDS	4CMC	5:1
10	SDS	5CMC	1:1
11	T80	0.5CMC	3:1
12	T80	1CMC	4:1
13	T80	2CMC	5:1
14	T80	4CMC	1:1
15	T80	5CMC	2:1
16	RL	0.5CMC	4:1
17	RL	1CMC	5:1
18	RL	2CMC	1:1
19	RL	4CMC	2:1
20	RL	5CMC	3:1
21	TX114	0.5CMC	5:1
22	TX114	1CMC	1:1
23	TX114	2CMC	2:1
24	TX114	4CMC	3:1
25	TX114	5CMC	4:1

* S/OS ratio: surfactant to oil sludge ratio.

The Taguchi design has all the levels balanced in each factor. In fact, each level of the surfactant type, surfactant concentration and S/OS ratio appears five times (Table 4.2). This static response-Taguchi design (no input signal) was obtained from Minitab 16 (Minitab Inc.). No input signal was considered because this was a preliminary experiment to test the factors and no previous data was available.

Since the aim of this study was to maximise the oil recovery, a Taguchi response tables for S/N ratios, mean and standard deviation were done using Minitab 16 (Minitab Inc.). Equation 4.2 was used to calculate the signal-to-noise ratios which find the factor that had the largest maximisation effect on the oil recovery.

$$S/N = -10 \times \log\left(\frac{\sum(1/Y^2)}{n}\right)$$

Equation 4.2. Signal-to-noise (S/N) ratio equation used to maximise the response variable (i.e. oil recovery rate).

where *Y* is the mean value and *n* is the number of trials for each experimental run (*n*=3). Moreover, a general linear model (GLM) was fitted to the obtained ORR data with effects for block and the different factors. Surfactant concentration and S/OS ratio (continuous variables) were included as covariates. This statistical test was Minitab 16 (Minitab Inc.) was used for the statistical analysis.

An experimental validation was performed to verify the robustness of the Taguchi design model. Prediction values of the oil recovery results were obtained using Minitab 16 (Minitab Inc.) by setting the parameters at the optimal levels per factor (i.e. at the maximum ORR % value) that resulted from the Taguchi design experiment. Then, these predicted results were compared with experimental results, and the percentage error was calculated. A percentage error less than 15% can validate the Taguchi design (Sivarao *et al.*, 2014).

4.3. Results

4.3.1. OSW parameters and the effect on the oil recovery

Figure 4.3 shows the three layers obtained after OSW which were the recovered oil and toluene layer at the top, a middle layer with water and surfactant, and a bottom layer of sediments from the sludge.

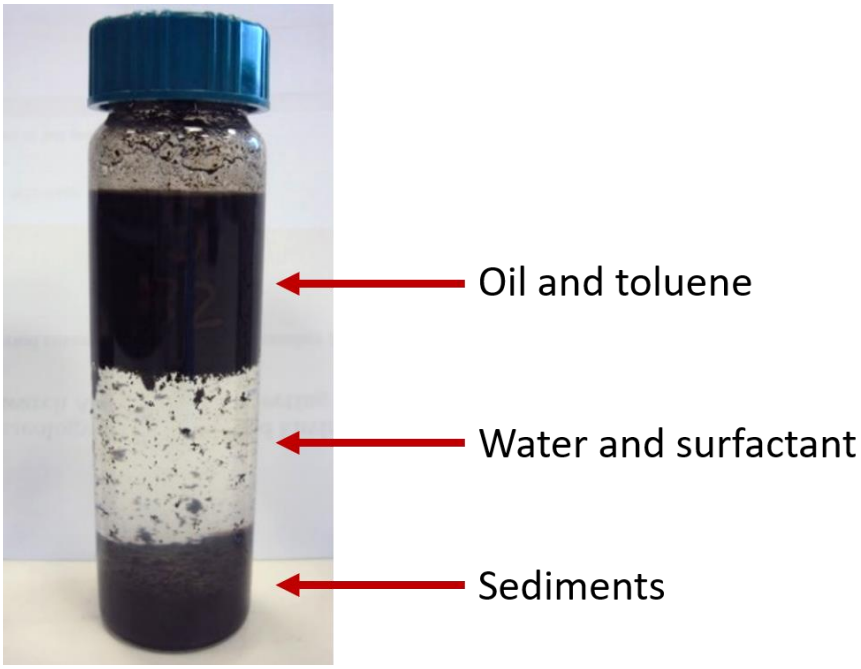

Figure 4.3. The final stage of the oil sludge washing process using TX100 (5CMC) at a 5:1 S/OS ratio.

The exploratory data analyses for the oil sludge washing test included bar charts of oil recovery rates (ORR %) and the surfactants used and its concentration (Figure 4.4) and ORR (%) values with different surfactants and S/OS ratios (Figure 4.5). The general linear model (GLM) results showed that there were highly significant differences among the Taguchi experimental design blocks (n = 5). Therefore, it was relevant to block the Taguchi design to account to this variation. There was an overall highly significant effect among all of these three factors ($p < 0.01$). Consequently, the two-way ANOVA evidenced highly significant differences in all the interactions among surfactant type and concentration, and S/OS ratio ($p < 0.01$). Regarding the main effects of each factor, only the surfactant type was highly significant ($p < 0.01$). However, there were not significant differences in the surfactant concentration and S/OS ratio factors ($p = 0.186$ and $p = 0.281$, respectively) among the Taguchi blocks.

These significant differences in the ORR among the types of surfactants can be based on the different nature of the surfactants. In fact, Chapter 3 discussed the variations in the micelle size, CMC, reduction of surface tension in water, surface activity, and chemical

structure for all the surfactants used in this thesis. For instance, since the surface activity (oil displacement test, Figure 3.8) was higher for the non-ionic surfactants (TX100, TX114, and RL), it was predicted that these surfactants would have a better performance in the oil recovery. In fact, these surfactants had higher ORR values compared to T80 and SDS as shown in Figure 4.4.

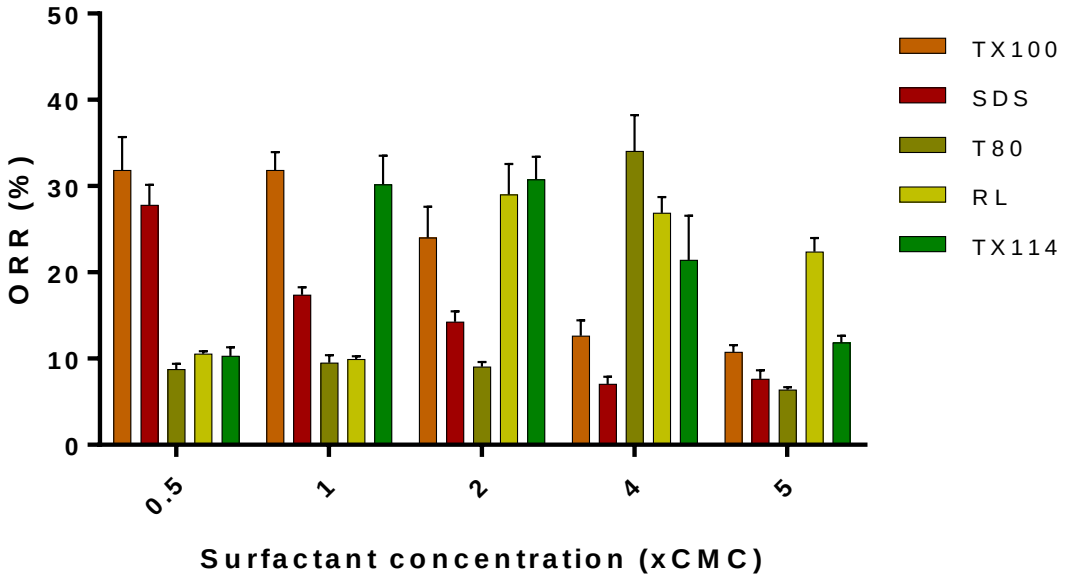

Figure 4.4. Oil recovery rate (%) with different surfactant types and concentrations. Concentrations are in terms of the CMC of each surfactant. The standard error of the mean (SEM) is shown in the bars (*n* = 5).

Figure 4.4 shows the mean of oil recovery for each type of surfactant and surfactant concentration. RL showed a 155% increase from 0.5CMC to 4CMC and a decrease in the ORR (%) value at 5CMC to 22% (±4). TX100 had its highest ORR value at 1 CMC, 32% (±5), and a 66% decrease from 1CMC to 5CMC. TX114 had an increase in the recovery values of 200% from 0.5CMC to 2CMC and a posterior 60% decrease to 5CMC. The highest percentage increase in ORR for RL and TX114 from the low to high concentrations implies that these surfactants favoured the solubilisation of the contaminant inside the micelles cores. This solubilisation can contribute to an enhancement of ORR above the CMC. On the contrary, SDS had a 75% decrease in the oil recovery rate value from 0.5CMC to 4CMC and an 8% increase at 5CMC. In fact, SDS was favoured by mobilisation of the contaminant by the surfactant

monomers because the highest ORR was obtained at concentrations below the CMC. The decrease in the ORR in all concentrations of SDS after the CMC probably show that the micellisation did not enhance the oil recovery. In fact, SDS had the smallest micelle size, 3.61 nm (Table 3.2; Section 3.3.1.1), which could affect the amount of solubilisate (contaminant) inside the micelle core of the SDS micelles.

T80 had not a clear pattern due to fluctuations in the oil recovery among concentrations. For instance, the ORR value ranged narrowly from 6% to 9% at 0.5, 1, 2, and 5 CMC, and the oil recovery rate was 34 % at 4CMC. This value was the highest compared to the other surfactants among all concentrations (Figure 4.4). This variability in the ORR among concentrations can be due to the high viscosity of T80 as discussed in Section 3.4.2. Therefore, this could affect the homogeneity of the surfactant solution at the different concentrations. In fact, it was mentioned before about the problem to estimate the CMC as this value was 100-fold higher than expected.

Figure 4.5 shows the ORR values per surfactant at different ratios to visualise better the differences among S/OS ratios. Even though the main effect of the S/OS ratio factor was not significant as mentioned before, the highest mean ORR values were found at low S/OS ratios (1:1 and 2:1). Then, a reduction in the oil recovery was observed from low to high S/OS ratios in all surfactants. The percentage reductions of ORR from 2:1 to 5:1 were 66%, 75%, 63%, and 66% for TX100, SDS, RL, and TX114, respectively. However, it was expected a higher ORR at higher S/OS ratios as more surfactant solution was added to the system.

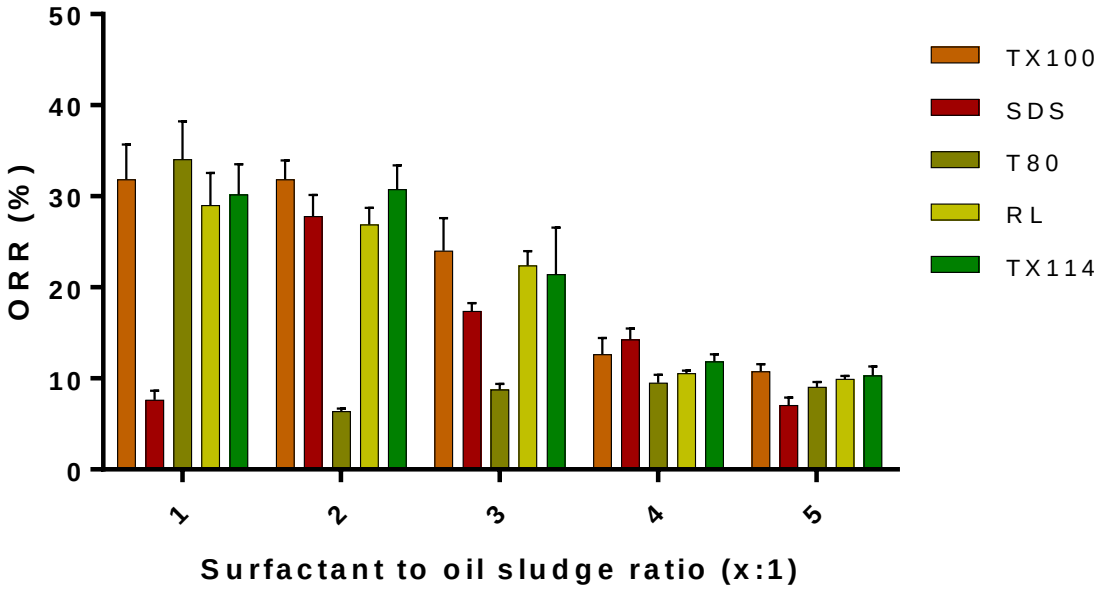

Figure 4.5. Oil recovery rate (%) with different surfactants and S/OS ratios. Concentrations are in terms of the CMC of each surfactant. The standard error of the mean (SEM) is shown in the bars (*n* = 5).

4.3.2. Maximisation of the oil recovery by the Taguchi experimental design

The importance of the Taguchi output is related to the selection of the best levels and factors that give the maximum ORR. By knowing this information, an OSW treatment plan can be proposed for this type of oil sludge sample in which the ORR can be optimised to have high oil recovery yields. Therefore, the response tables of signal-to-noise (S/N) ratios, means and standards deviations can be used for this purpose because these tables rank the ORR data from minimum to maximum values among the factors and levels. Table 4.3 shows the signal-to-noise ratios, means and standard deviations of each factor with the delta values (Δ = Highest S/N ratio – Lowest S/N ratio) and the rank obtained in each case. In addition, these tables give information on which factor can be used to reduce the variation in the ORR, so the factor with the highest effect (1st rank) on the mean and standard deviation can be used for this purpose. By reducing the variation in the ORR response, the OSW process can be more robust (Wysk *et al.*, 2000). The factor with the highest effect on the S/N ratio can be used to obtain the

maximum ORR. In this study, the S/OS ratio was the factor with the highest effect on the maximisation of ORR with toluene as co-solvent in all the S/N ratios, means and standard deviations. In fact, the main effects plots for S/N ratios, means and standard deviations indicated that the S/OS ratio had the highest influence on the S/N ratio (7.4), mean (17.1%) and standard deviation (5.5%) from the oil recovery rates (Table 4.3).

Table 4.3. Delta (Δ) values and ranks from the Taguchi design's response tables of S/N ratios, means and standard deviations of each factor for the maximisation of ORR.

	Surfactant		***Surfactant Concentration***		***S/OS Ratio*[2]**	
	Delta	*Rank*	*Delta*	*Rank*	*Delta*	*Rank*
S/N ratios[1]	4.8	2	4.7	3	7.4	1
Means	8.7	3	9.6	2	17.1	1
Standard deviations	3	3	4.1	2	5.5	1

[1] *S/N:* Signal-to-noise ratios.
[2] S/OS *Ratio:* Surfactant to oil sludge ratio.

Table 4.4 to Table 4.6 shows the response tables for all the levels of each factor. Table 4.4 shows the response table for S/N ratios for the maximisation of oil recovery; Table 4.5 presents the table for means and Table 4.6 for the standards deviations. Briefly, TX100 (9.5), RL (9.7), and TX114 (9.5) had greater effects on S/N ratios than SDS (7.8) and T80 (7) as shown in Table 4.4. Concentrations with higher effects on S/N ratios corresponded to 1CMC (9.4) and 4CMC (9.3). However, this high value for 4CMC was due to the high ORR value obtained for T80 at this concentration. Also, Table 4.4 shows that S/N ratios for the S/OS ratios were higher at 1:1 (11.4). TX100 and RL (both with 3.3), 1 and 4CMC (3.1 and 3.2, respectively), and 1:1 and 2:1 S/OS (3.8 and 3.7, respectively) had the largest effects on the mean ORR (Table 4.5). T80 (0.8), 2CMC (0.8) and 3:1 S/OS (0.9) had the highest impact changing the standard deviation of the oil recovery values (Table 4.6). These standard deviation values calculated by the Taguchi method were obtained from each combination of factors (Minitab, 2014). The relevance of these data is that the 1:1 S/OS ratio can be selected for this oil sludge sample to maximise the ORR and reduce the variation in the system. Therefore, the OSW method can be more robust.

Table 4.4. Response table of the S/N ratios for the maximisation of ORR. Each level number per factor (surfactant, surfactant concentration, and S/OS ratio) is explained in Table 4.6. The higher the number (in bold), the higher the effect.

Level	*Surfactant*	*Surfactant Concentration*	*S/OS Ratio*
1	**9.5**	8.7	**11.4**
2	7.8	**9.4**	10.4
3	7	8.1	9.4
4	**9.7**	**9.3**	6.1
5	**9.5**	8	6.2
Delta (Δ)	2.8	1.4	5.3
Rank	2	3	1

Table 4.5. Response table of the means for the maximisation of ORR. Each level number per factor (surfactant, surfactant concentration, and S/OS ratio) is explained in Table 4.6. The higher the number (in bold), the higher the effect.

Level	*Surfactant*	*Surfactant Concentration*	*S/OS Ratio*
1	**3.3**	3	**3.8**
2	2.7	**3.1**	**3.7**
3	2.7	3	3.4
4	**3.3**	**3.2**	2.1
5	3.2	2.8	2.1
Delta (Δ)	0.6	0.3	1.7
Rank	2	3	1

Table 4.6. Response table of the standard deviations for the maximisation of ORR. Each level number per factor (surfactant, surfactant concentration, and S/OS ratio) is explained in Table 4.6. The higher the number (in bold), the higher the effect.

*Level**	*Surfactant*	*Surfactant Concentration*	*S/OS Ratio*
1	0.5	0.5	0.5
2	0.6	0.3	0.7
3	**0.8**	**0.8**	**0.9**
4	0.3	0.5	0.3
5	0.4	0.6	0.2
Delta (Δ)	0.5	0.5	0.7
Rank	3	2	1

Levels explained **Type of surfactant:** **1** = TX100, **2** = SDS, **3** = T80, **4** = RL, **5** = TX114
Surfactant concentration: **1** = 0.5CMC, **2** = 1CMC, **3** = 2CMC, **4** = 4CMC, **5** = 5CMC
Surfactant to oil sludge ratio: **1** = 1:1, **2** = 2:1, **3** = 3:1, **4** = 4:1, **5** = 5:1

In summary, the optimal level for oil recovery maximisation per factor was 1:1 S/OS ratio, 2CMC of surfactant concentration, and TX100. 1CMC level also had a high S/N ratio that maximised ORR values. Also, RL and TX114 showed a maximisation effect with S/N ratios similar to TX100.

Figure 4.6 shows the overall mean of ORR% at the different levels of each factor to summarise all these findings and to illustrate how the Taguchi method maximised each factor.

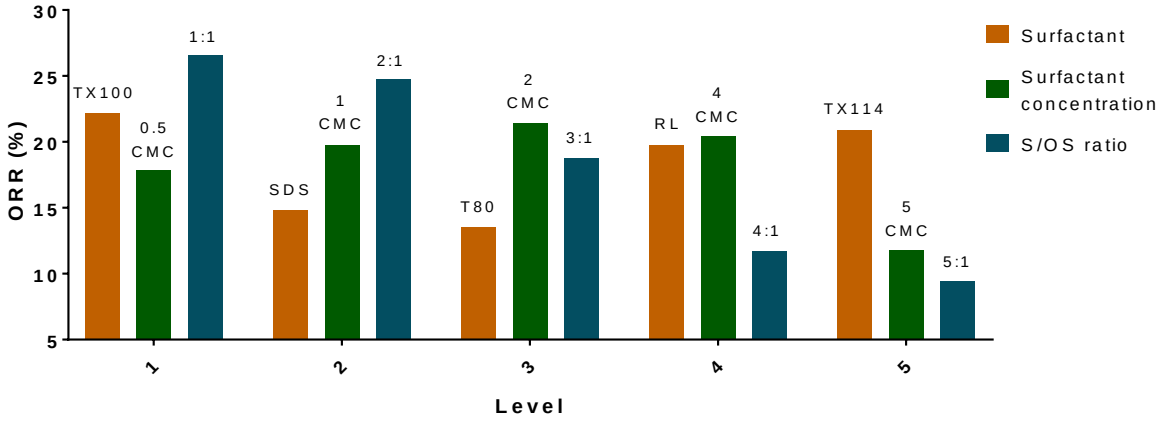

Figure 4.6. Overall performance in the percentage of oil recovery rates (ORR %) of individual factors at different five levels based on the Taguchi response table for means. Type of surfactant: 1 = TX100, 2 = SDS, 3 = T80, 4 = RL, 5 = TX114. Surfactant concentration: 1 = 0.5CMC, 2 = 1CMC, 3 = 2CMC, 4 = 4CMC, 5 = 5CMC. Surfactant to oil sludge ratio: 1 = 1:1, 2 = 2:1, 3 = 3:1, 4 = 4:1, 5 = 5:1.

Mean predicted ORR values were compared to the observed Taguchi ORR results for testing the robustness of the Taguchi design (Table 4.7). The optimal levels (1:1 S/OS and 2CMC) obtained with the Taguchi method and the surfactants with the highest oil recovery values (RL, TX100 and TX114) were analysed. All mean percentage errors were below the 15% threshold supporting the robustness of the Taguchi design except for RL at 1CMC and 1:1 S/OS ratio with a percentage error higher than 15% (23%).

Table 4.7. Mean predicted and observed Taguchi results for RL, TX100 and TX114 at 1CMC and 2CMC for 1:1 S/OS ratio.

Factors			Mean[1]		
Surfactant	***Concentration***	***S/OS Ratio***	***Predicted***	***Observed***	***Error (%)[2]***
RL	1CMC	1:1	30	36	23
TX100	1CMC	1:1	32	36	13
TX114	1CMC	1:1	30	32	5
RL	2CMC	1:1	31	34	8
TX100	2CMC	1:1	34	35	5
TX114	2CMC	1:1	32	37	15

[1] Predicted and observed values correspond to the of mean ORR (%) (n = 3).
[2] Error (%): Percentage error = | (Observed - Predicted) / Predicted | × 100%

4.4. Discussion

4.4.1. Performance of the surfactants in the oil recovery

In this study, the amount of oil recovered by the surfactants was higher for RL, TX114 and TX100; they had higher surface tension reduction in water (and low CMC) compared to SDS and T80. Low surface and interfacial tensions are preferred in the petroleum industry for improvement of oil recovery yields (Austad and Milter, 2000). The high oil recovery values for RL, TX114 and TX100 can also be related to their low hydrophilic/lipophilic balance (HLB) numbers (9.5, 12.4, and 13.5, respectively) as a high oil extraction was obtained due to their high hydrophobicity (Kwon and Lee, 2015). On the contrary, SDS and T80 had low amounts of recovered oil and higher surface tension reduction values. The low recovery values for T80 could be associated with its higher molecular weight (1,309.68 $g \cdot mol^{-1}$). Finch (1995) reported that this is a factor that could lead to micelle instability and detergency reduction due to changes in the micelle shape and size.

RL, TX114, and TX100 had higher surface activities than SDS and T80 according to the oil displacement test done in Chapter 3 of this thesis (Section 3.3.1.3). Therefore, the oil displacement test was a good predictor of the performance in the oil recovery as these surfactants had the highest amount of recovered oil as mentioned before. When comparing the surface activity of surfactants (oil displacement test) with ORR values (OSW), there was an inverse relationship between these values. For example, TX100 had an increase in the areas of

the clear zones with increasing concentrations of surfactants, but the recovered oil was higher at lower concentrations of surfactant. Also, this was the trend for SDS, which had higher surface activities at higher concentrations, but the greater amount of recovered oil was at lower concentrations. For RL, larger areas of the clear zones were evidenced at lower concentrations, whereas the highest levels of recovered oil were at higher concentrations. The inverse relationship between oil displacement test and oil recovery data could indicate that the physicochemical nature of the sample matrix (e.g. oil sludge) could influence either the mobilisation (below CMC) or solubilisation (above CMC) of the oil. Therefore, the chemical interaction between the surfactant monomers or micelles and the sludge matrix is possibly dictating this preference of recovery below of above of CMC. For instance, the charged nature of the anionic SDS could be affecting the interaction with the sludge and consequently giving the low ORR values.

4.4.2. Micelle size and the effect on oil recovery

When micelles are solubilising the hydrocarbons into the hydrophobic micelle core, the micellar aggregation number can increase. This aggregation number corresponds to the number of surfactant monomers per micelle (Schramm, 2000a). Due to this growth in the aggregation number, the micelle can solubilise more hydrophobic material inside its core until the solubilisation limit is reached (Rosen and Kunjappu, 2012). According to this premise, different aggregation numbers in the micelles can influence the amount of hydrocarbons captured by the micelle. For instance, TX100 (100-155) has a higher aggregation number (Table 3.1) compared to T80 (60) and SDS (60-70). Consequently, TX100 had a higher oil recovery than SDS and T80 (Figure 4.7).

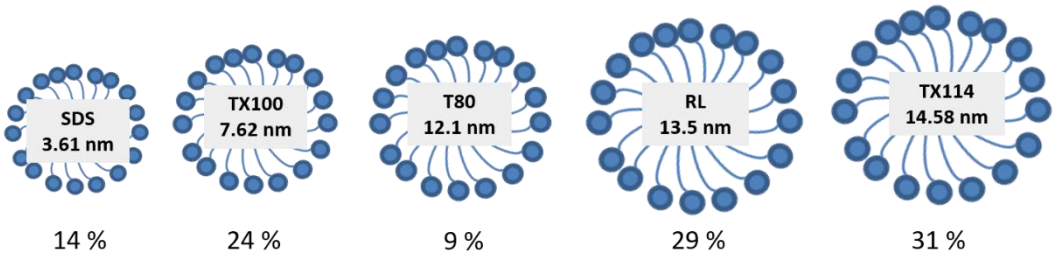

Figure 4.7. Comparison between micelle sizes (Table 3.2) and the ORR values at 2CMC (Figure 4.4) for the used surfactants.

In general, oil recovery values can be related to the degree of solubilisation of oil hydrocarbons. Since the oil hydrocarbons are solubilised inside the micelle core (hydrophobic part), there was a trend in this study that large micelle sizes contribute to high amounts of solubilised oil hydrocarbons than small micelles (Figure 4.7). This high solubilisation was the case for TX114 and RL which had the largest sizes and best performance in the oil recovery. According to Rosen and Kunjappu (2012), an increase in the micelle size contributes to a high amount of oil hydrocarbons solubilised into the micelle core. T80 also had a large micelle, but the oil recovery was lower except at 4CMC which was the highest oil recovery value obtained in this study. Also, the oil recovery using T80 fluctuated among the concentrations probably due to its high molecular weight, viscosity, and impurities presented as mentioned in Chapter 3. Indeed, this could affect the homogeneity of the T80 solution. Despite the small micelle size of TX100, the amount of recovered oil was high. The small size of the SDS micelle was consequent with its low recovery values (Figure 4.7).

4.4.3. Taguchi experimental design to maximise the oil recovery

The obtained Taguchi results showed that the S/OS ratio is a critical factor because it had the largest effect on the maximisation of oil recovery (S/N ratios), the average and the standard deviations (Figure 4.6). Higher recoveries were obtained at low S/OS ratio levels, whereas low recoveries were found at high levels of S/OS ratio. There are no reports to date supporting the high oil recovery at low surfactant to soil or sludge ratios. In fact, this finding for the S/OS ratio does not support the results found by Peng et al. (2011) and Wu et al. (2012) in soil

washing parameters studies. These authors reported that higher PAH removal was achieved at higher ratios due to a greater capacity of solubilisation as more surfactant was added. The higher ORR at lower ratios could be due to the washing time (one hour) that was not enough to reach the thermodynamic equilibrium to recover all the oil when more surfactant solution is added to the system. Also, it could occurred that all the possible amount of oil was recovered from this specific sludge at low S/OS ratios, so higher ratios are not necessary to enhance the OSW process. Also, Zubaidy and Abouelnasr (2010) reported a similar situation in their solvent extraction studies, where they found a decrease from 4:1 C/OS to 6:1 C/OS ratios in the oil recovery using only MEK and LPG condensate. In fact, they proposed that this decrease could be due to the reasons mentioned above.

According to the Taguchi experimental design results, the maximum oil recovery from this sludge sample was obtained above the CMC (2CMC), so the oil hydrocarbons were solubilised. However, Urum and Pekdemir (2004) and Deshpande et al. (1999) reported in their soil washing studies a maximum oil removal from soil at lower concentrations than the CMC due to the mobilisation of the contaminant. Indeed, the ORR values will depend on the sludge matrix as mentioned before. In fact, Deshpande et al. (1999) had concluded in their study that since the surfactants had different behaviour in the different soil and contaminant matrices, it is important to do a bench-scale test for the selection of surfactants in a specific sludge matrix.

4.4.4. Validation of the Taguchi experimental design

The robustness of the Taguchi design performed was assessed using the parameters that had high oil recovery values (Table 4.7). The mean percentage errors were below the 15% threshold (Sivarao *et al.*, 2014). These values supported the Taguchi model used in this study. The Taguchi results obtained can contribute to the setting of optimal conditions for maximising the oil recovery. Therefore, since the S/OS ratio had the highest effect on the mean and standard deviation, this factor can be used to reduce the variation in the system (Wysk *et al.*, 2000) by selecting the optimal ratio for this sludge (low ratio, 1:1).

4.5. Conclusions

The results of this study suggested that less surfactant can be used (lowest ratio 1:1 and low concentration, 2CMC) for the maximum oil recovery from this type of oil sludge, minimising costs. However, since there were no reports to date supporting high oil recovery at lower ratios, it is suggested to test different types of oil sludges.

The surfactants that had a better performance in the recovery were TX100, RL and TX114, and this could be confirmed with the oil displacement test results from Chapter 3. In fact, these surfactants had the highest surface activities. Also, their micelles were larger and the aggregation numbers were higher which potentially contributed to higher oil recoveries. The Taguchi method approach for the experimental design was suitable to establish the optimal parameters due to the number of factors involved (surfactant type, surfactant concentration and S/OS ratio). The S/OS ratio had the strongest effect on the maximisation of the oil recovery, average and standard deviations. By selecting the lowest S/OS ratio (1:1) in the OSW of this sludge from an oil-water separator, the variation can be reduced, and the oil recovery can be maximised. Moreover, the Taguchi experimental design was robust as proven by comparing experimental with expected data.

Since this was a preliminary study with only one sludge, it is necessary to test more samples to see the differences in the oil recovery among oil sludges from different sources.

Chapter 5 - Co-solvent and surfactant mixture effect on the oil recovery from an oil-water separator sludge

5.1. Introduction

In the previous chapter, an initial evaluation of the optimal OSW parameters in the oil recovery from the WSS sludge was performed. It was established that the S/OS ratio had the strongest effect in maximising the recovery. The surfactants with the best recoveries were TX100, RL, and TX114, and the overall optimal concentration was 2CMC. Toluene was used as a co-solvent in the last chapter as suggested before (El Naggar *et al.*, 2010; Atta and Elsaeed, 2011). As mentioned before in Chapter 4, El Naggar et al. (2010) reported that this was the best solvent to recover hydrocarbons from sludge (76%) compared to the other solvents evaluated (*n*-heptane, methylene and ethylene dichloride, diethyl ether, and naphtha and kerosene cut). In addition, toluene was used as a carrier of different solutions of non-ionic surfactants to treat oil sludge (Atta and Elsaeed, 2011). Also, it has been used to reduce the viscosity of crude oil (Jennings Jr and Abou-Sayed, 1994), and it is an efficient oil extractant from heat-treated oil shales (Bock *et al.*, 1984). Despite the efficiency and common use of toluene in oil recovery studies, it is not considered to be benign to the environment and health (Fishbein, 1985; Young, 2007b). Therefore, it is necessary to test alternative other organic co-solvents that are less harmful to the environment.

The rationale behind the use of a co-solvent in the oil recovery is the selective extraction of all oil components from sludge, and therefore, the miscibility of solvent with the oil is determinant in the success of the oil extraction (Rincón *et al.*, 2005a). Also, these authors emphasised that the solvent must repel chemical additives used in the oil industry and also the dispersed particles from the oil/solvent solution. Then, the sedimentation of unwanted particles by gravitation can be facilitated (Rincón *et al.*, 2005a). As mentioned before, both polar and non-polar co-solvents are used in the oil recovery depending on the chemical nature of the matrix (Jafvert, 1996); this idea follows the "like dissolves like" principle (Hansen, 2007). Oil sludges are complex matrices with mostly hydrophobic contaminants such as oil hydrocarbons. Therefore, hydrophobic organic co-solvents (e.g. hexane and toluene) are preferred over alcohols due to the better performance of the former solvents in the solubilisation of oil (Jafvert, 1996).

The co-solvents chosen for this chapter are divided into two groups: cyclic and aliphatic linear chain compounds. Cyclic hydrocarbons included cyclohexane and one aromatic compound, toluene; whereas the three aliphatic linear chain compounds were *n*-pentane, *n*-hexane, and one branched aliphatic compound, isooctane. The physicochemical properties of the co-solvents used in this study and their toxicity status are shown in Table 5.1.

Table 5.1. Description of the co-solvents used in this study.

Co-solvent	Formula	MW [1]	Water solubility	log K_{ow} [2]	Melting point	HSP (δ) [3]	Toxic properties and environmental impact [4]				
		g·mol^{-1}	*mg·l^{-1}*		*°C*	*MPa^{½}*	Waste	Environment	Human health	Flammability	Reactivity
***n*-pentane**	C_5H_{12}	72.15	40	3.39	-130	14.5	5	6	8	2	10
***n*-hexane**	C_6H_{14}	86.17	9.5	4.11	-96	14.9	5	3	4	2	10
Toluene	C_7H_8	92.14	520	2.7	-95	18.2	6	3	4	4	10
Cyclo-hexane	C_6H_{12}	84.16	Immiscible	3.44	6.47	16.8	5	5	7	2	10
Iso-octane	C_8H_{18}	114.23	Immiscible	5.18	-107	14.3	6	4	8	3	10

All physicochemical data were retrieved from the *ChemSpider database* http://www.chemspider.com/ (Royal Society of Chemistry, 2016), except for the Hildebrand solubility parameters (HSP) of all solvents Hansen (2007).

[1] Molecular weight (MW).

[2] Octanol-water partition coefficient (K_{ow}).

[3] Hansen solubility parameter (HSP): Hansen (2007).

[4] Solvent toxicity and environmental issues were established in the *GlaxoSmithKline (GSK) Solvent Selection Guide* on 2009 (Royal Society of Chemistry, 2010). Impact score from 1 to 3 (red; high impact) to 8-10 (green; low impact) (Henderson *et al.*, 2011). *Waste*: Recycling, incineration, volatile organic compounds (VOC), and biotreatment issues. *Environment*: Fate and effects. *Health*: exposure potential; acute and chronic effects on human health. *Flammability*: Storage and handling. *Reactivity*: Factors affecting the stability of the solvent (Henderson *et al.*, 2011).

All the co-solvents analysed in this experimental chapter have been used in chemical analyses and extractions of non-polar substances. However, pentane and hexane have red flags in the Environmental, Health and Safety (EHS) legislation; and toluene has been suggested to be substituted with other solvents with less hazard (Henderson *et al.*, 2011). Toluene, toluol or methylbenzene (Young, 2007b) is a mono-substituted aromatic with a CH_3 group connected to the benzene ring structure. It can be obtained from the catalytic reforming process in the petroleum refining by the dehydrogenation of specific naphthalene-containing petroleum fractions (Fishbein, 1985). The other cyclic compound used in this study is cyclohexane which is also known as hexamethylene (Young, 2007a). Physicochemical properties of cyclohexane such a melting and boiling points are higher than its corresponding alkane (i.e. hexane) (Roberts and Caserio, 1977).

n-hexane or hexyl hydride (Young, 2001), one of the aliphatic co-solvents used, has a saturated straight-chain. According to the Canadian Council of Ministers of the Environment (CCME, 2011), this solvent is found in crude oil and natural gas, and it is used as a degreaser in some industries (e.g. paint, textile, leather). *n*-pentane is used in solvent extraction processes, as a blowing agent in plastics, and in pesticides (Milne, 2005). The only branched aliphatic compound used in this study was isooctane. Also known as 2,2,4-trimethylpentane, is a petroleum product from the refinery and used as a solvent in chemical analysis (Patnaik, 2007).

Solubility parameters are useful to distinguish solvents. The Hansen solubility parameter (HSP) (1967) is a commonly used value to predict the dissolution of a specific material into another one. This parameter includes three components in the system which come from the energy from dispersion (London) forces (E_d), dipolar intermolecular forces (E_p), and hydrogen bonds (E_h) between molecules (Hansen, 1969). By dividing each component by the molar volume of the solvent, the final equation that determines the HSP is shown in Equation 5.1.

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

Equation 5.1. The Hansen Solubility Parameter (HSP)

Each parameter corresponds to the cohesive energy density, where δ_d^2 corresponds to the dispersion London forces, δ_p^2 to the dipolar intermolecular forces, and δ_h^2 to the hydrogen bonding between molecules. The units for all the components are in $MPa^{½}$. These values can be used to explain the behaviour of the solvents in the oil recovery process (Hansen, 1969). The Hansen solubility parameters for the co-solvents at 25 °C are shown on Table 5.1.

Table 5.1 shows the log K_{ow} values of each solvent. The octanol-water partition coefficient (K_{ow}) is a dimensionless concentration ratio of a specific chemical substance in equal volumes of two partially mixable solvents (*n*-octanol and water) (Witkowski *et al.*, 1987; Pontolillo and Eganhouse, 2001). Log K_{ow} is a commonly used hydrophobicity parameter, so this will dictate if the solvent will partition to the octanol (hydrophobic) or the water (hydrophilic) (Reichardt, 2004). Moreover, if the log K_{ow} is high, the compound is considered to be more non-polar. For instance, *n*-hexane and isooctane are the co-solvents with the highest log K_{ow} in this study (Table 5.1).

So far in this thesis, the oil recovery has been analysed gravimetrically. Moreover, the total EPH concentrations in the recovered oil can be analysed. In fact, Chapter 2 mentioned the importance of characterising the aliphatic and aromatic fractions in the oil sludge and the recovered oil. Therefore, this information can assess the potential use of the oil from the sludge mixture as a feedstock for fuel production. For instance, a recovered oil with a high presence of light aliphatic fractions can be used as a source of diesel (Giles, 2010).

This chapter also assesses the oil recovery when two surfactants are combined. As mentioned in the literature review (Chapter 2, Section 2.11), surfactant mixtures have been used in EOR processes to increase the solubilisation of the oil and improve the performance in the oil recovery (Ghosh, 2001; Chatterjee *et al.*, 2006; Hirasaki *et al.*, 2011; Sahu *et al.*, 2015). This enhancing effect in the oil recovery occurred when there is synergy in the surfactant mixture. For example, a synergistic effect can be the decrease of the critical micelle concentration (CMC) of each surfactant in the mixture (Antón *et al.*, 2008).

This study aims to test the effects of different co-solvents with various degrees of toxicity (toluene, cyclohexane, hexane, pentane and isooctane) in the oil recovery during the OSW of the WSS sludge. Since the OSW parameters were optimised on Chapter 4, RL, TX100 and TX114 added at 2CMC and 1:1 S/OS were used in this experiment. The second objective of

this study is to evaluate the effect of using surfactant mixtures in the oil recovery. All possible combinations were evaluated with all the surfactants used in this thesis.

5.2. Materials and Methods

5.2.1. Oil sludge

Oil sludge (WSS as named in Chapter 2) was sampled in England. The oil sludge was taken at the oil/water separation step in an oil refinery process. The total extractable petroleum hydrocarbons (EPH) concentration was 33,000 (±3,000) ppm, which 31,000 (±2,000) ppm and 2,000 (±800) ppm corresponded to the total aliphatic fraction (C_{10}-C_{36}) and aromatic fraction (C_{11}-C_{22}), respectively. A higher concentration in the C_{10}-C_{18} aliphatic fraction was found (20,000 (±900) ppm) compared to the C_{19}-C_{36} aliphatic fraction (11,000 (±1,300) ppm). The sludge was viscous and black. It has a semi-solid cake state at room temperature. For more physicochemical characteristics, see Chapter 3 (Section 3.3.2). This sludge was the same used in the oil sludge (OSW) parameters experiment (See Chapter 4). The oil sludge washing process followed the procedure mentioned in Chapter 4 (Section 4.2.3)

5.2.2. Co-solvents

n-pentane, *n*-hexane, toluene, cyclohexane, and isooctane were high-purity (HPLC grade) solvents (Fisher Scientific).

5.2.3. Co-solvent effect

Three surfactants [Triton X-100 (TX100), 90% pure rhamnolipid with 5% liquid (RL), Triton X-114 (TX114)] were selected due to their optimal performance in the maximisation of oil recovery on the preliminary OSW study of the oil-water separator sludge (See Chapter 4). RL was obtained from AGAE Technologies (Corvallis, Oregon, USA), and TX114 and TX100

were laboratory grade and supplied by Sigma-Aldrich. All concentrations needed for this study were prepared from an intermediate stock solution of 10% (w/v) RL and 10% (v/v) of TX100 and TX114 dissolved in ultrapure water (18.2 MΩ·cm) at room temperature (20 °C).

A full-factorial design experimental design (Table 5.2) was applied with three factors: Surfactant (TX100, RL and TX114), co-solvent (toluene, cyclohexane, hexane, pentane, and isooctane) and co-solvent to oil sludge ratio, C/OS, (1:1, 2:1).

Table 5.2. Factors and levels of the experimental design for the co-solvent effect experiment.

Surfactant	Co-solvent	C/OS ratio
Triton X-100 (TX100)	Pentane	1:1
90% pure rhamnolipid (RL)	Hexane	2:1
Triton X-114 (TX114)	Toluene	
	Cyclohexane	
	Isooctane	

Since the purpose of this study is to find an alternative co-solvent to toluene, this factor had more levels (5), so the surfactant and C/OS ratio factors can have a minimum number of levels to decrease the number of experimental runs as possible. This experiment was done in triplicate with a total of 30 experimental runs per replicate. Two response variables were analysed, the recovered amount of oil (ORR %) and the EPH concentrations in the recovered oil (ppm). The EPH extraction (Section 3.2.2.4), SPE clean-up with separation of aliphatic and aromatic compounds (Section 3.2.2.5), and EPH analysis (Section 3.2.2.6) with the MADEP method (2004) of the recovered oil and the OSW residuals were described in Chapter 3. A three-way ANOVA was performed on the data with effect of surfactant type, co-solvent type and C/OS ratio. Paired t-tests (α=0.05) were done to compare the means between co-solvents. The statistical analyses were done using Minitab 17.3.1 (Minitab Inc.). The graphs were done with GraphPad Prism 7 for Windows (GraphPad Software, Inc.).

5.2.4. Surfactant mixture effect

All surfactants were combined in pairs at a 1:1 surfactant to surfactant (v:v) ratio. This fixed ratio was selected to have the surfactants in equal proportions (El-Batanoney *et al.*, 1999; Chatterjee *et al.*, 2006), and also another variable can be removed to avoid any increase in the number of experimental runs. As mentioned before (Section 2.11), a 1:1 surfactant mixture ratio can be a breakpoint between antagonistic and synergistic effects in a surfactant mixture (Chatterjee *et al.*, 2006). Each surfactant was added at 2CMC and 1:1 S/OS ratio because these were the optimal parameters in the preliminary OSW study (See Chapter 4). The surfactant mixture was added at a 1:1 S/OS ratio. The response variable was the recovered amount of oil (ORR %). A one-way analysis of variance was performed on the data with effects for the surfactant mixture using Minitab 17.3.1 (Minitab Inc.). Furthermore, multiple t-tests (α=0.05%) were done per surfactant (RL, TX100, TX114) to compare the means between the ORR data from the co-solvent and the surfactant mixture effect experiments. These tests were done to see if there was an improvement in the recovery by using surfactant mixtures. The graphs were done with GraphPad Prism 7 for Windows (GraphPad Software, Inc.).

5.3. Results

5.3.1. Effect of the co-solvents in the concentrations of oil fractions from the recovered oil layer

The three-way ANOVA revealed that there were not significant differences among the co-solvent type, surfactant, and C/OS ratio factors on the total EPH concentrations of the recovered oil ($p = 0.973$). The only factor with highly significant effects was the co-solvent type ($p < 0.01$). Although higher concentrations of EPH were obtained at 1:1 C/OS than 2:1 C/OS, the difference was not significant ($p = 0.139$) (Figure 5.1). Pentane, hexane, and isooctane recovered a higher concentration in each oil fraction compared to cyclohexane and toluene (Figure 5.1). TX100 had the highest EPH total concentrations with hexane at 2:1 C/OS ratio (21,000 (±5,100) ppm) and pentane at 1:1 C/OS ratio, 20,500 (±4,400) ppm. Also, RL and hexane at 1:1 C/OS ratio contributed to the recovery of a high EPH concentration, 20,100

(±3,300) ppm. The lowest total EPH concentration was 12,700 (±4,000) ppm when RL and cyclohexane (2:1 C/OS) were mixed.

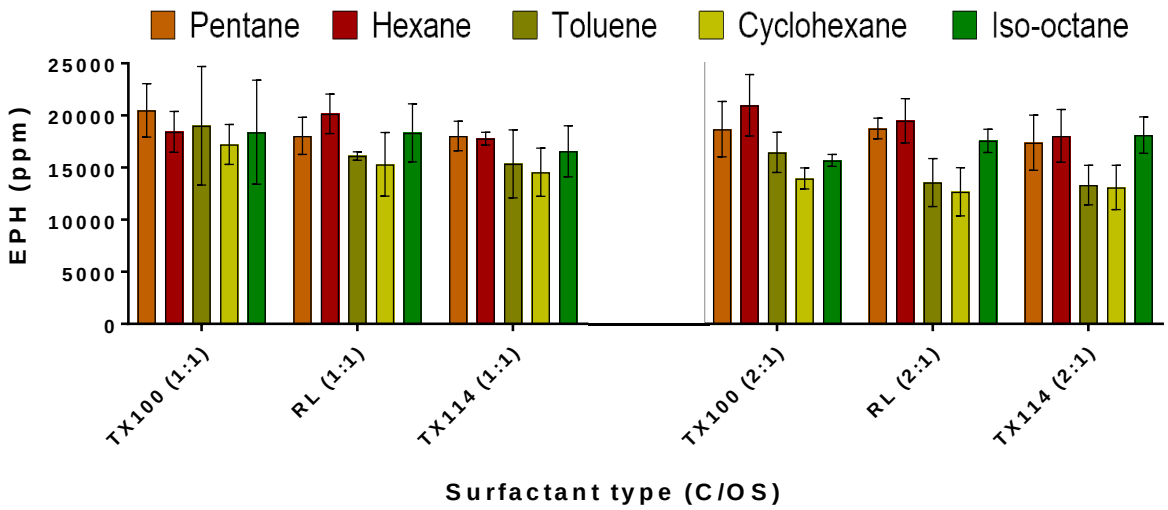

Figure 5.1. Total extractable petroleum hydrocarbons (EPH) concentration values for the different co-solvents, C/OS ratios, and surfactants. The standard error of the mean (SEM) bars are shown (*n* = 3).

Figure 5.2 shows only the mean values of each aliphatic and aromatic oil fraction for all the treatments. The mean value of the C_{10}-C_{18} aliphatic fractions was between 55% (TX100, toluene, 1:1 C/OS ratio) to 59% (RL, pentane, 2:1 C/OS ratio) of the total EPH concentrations values. For C_{19}-C_{36} aliphatic fraction, the mean value was between 37% (TX114, hexane, 2:1 C/OS ratio) to 41% (TX100, toluene, 1:1 C/OS ratio). The C_{11}-C_{22} aromatic fraction ranged from 4% (RL, toluene, 1:1 C/OS ratio) to 6% (TX114, cyclohexane, 1:1 C/OS ratio).

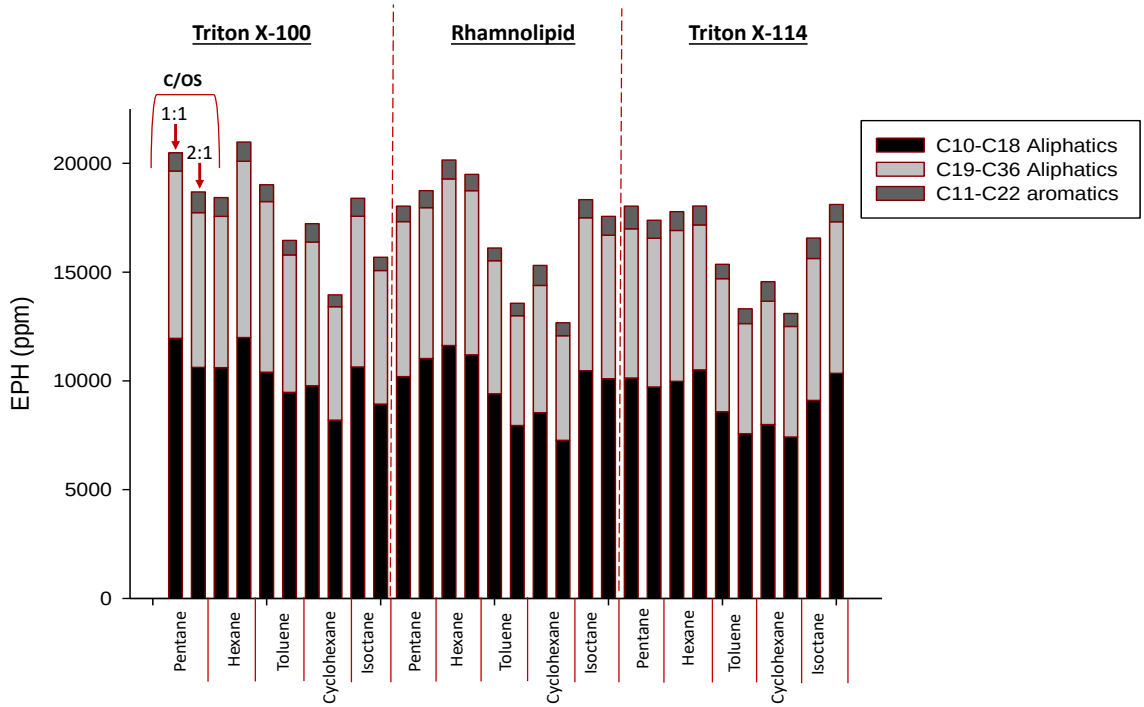

Figure 5.2. Comparison of the three fractions (C_{10}-C_{18} and C_{19}-C_{36} aliphatics and C_{11}-C_{22} aromatics) of the total extractable petroleum hydrocarbons (EPH) values. Each solvent is represented by two bars at 1:1 C/OS (left) and at 2:1 C/OS (right) ratios.

The total aliphatic fractions (C_{10}-C_{36}) obtained from the recovered oil layer samples showed that the highest EPH concentration values in the C_{10}-C_{18} and C_{19}-C_{36} aliphatic fractions were 12,000 (±2,800) ppm and 8,100 (±2,300) ppm, respectively. These values were obtained when TX100 and hexane at a 2:1 C/OS ratio were used. On the contrary, the lowest values were 7,300 (±3,100) ppm and 4,800 (±950) ppm in the C_{10}-C_{18} and C_{19}-C_{36} aliphatic fraction, respectively, when RL and cyclohexane at a 2:1 C/OS ratio were added.

TX114 and pentane at 1:1 C/OS ratio had the highest value for the C_{11}-C_{22} aromatic fraction, 1,000 (±500) ppm. The lowest EPH concentration value for the C_{11}-C_{22} aromatic fraction was 550 (±160) ppm with TX100 and cyclohexane at a 2:1 C/OS ratio.

5.3.2. Effect of different co-solvents in the oil recovery

In general, a three-way ANOVA evidenced an overall highly significant effect of the co-solvent type, surfactant, and C/OS ratio on the ORR ($p=0.015$). Consequently, there were highly significant statistical differences at a two-way interaction level between the co-solvent type and C/OS ratio ($p<0.01$). The factors with the highly significant effects were the solvent type and C/OS ratio (both $p<0.01$). In fact, ORR values were higher at 2:1 C/OS ratio than 1:1 C/OS (Figure 5.3). The type of surfactant did not have a significant effect on the oil recovery ($p = 0.396$).

The highest ORR values [73% (±4) and 64% (±9)] were obtained with toluene at a 2:1 C:OS ratio using TX100 and RL, respectively. Cyclohexane also had high recovery values at 2:1 C/OS ratio with RL and TX114, 63% (±2) and 63% (±3), respectively. Overall, toluene was not significantly different from cyclohexane in all the combinations of surfactant type and C/OS ratios ($p=0.62$). Specifically, multiple t-tests ($\alpha=0.05$) revealed that only there were highly significant differences in the RL at 1:1 and TX100 at 2:1 treatments ($p = 0.026$ and $p = 0.037$).

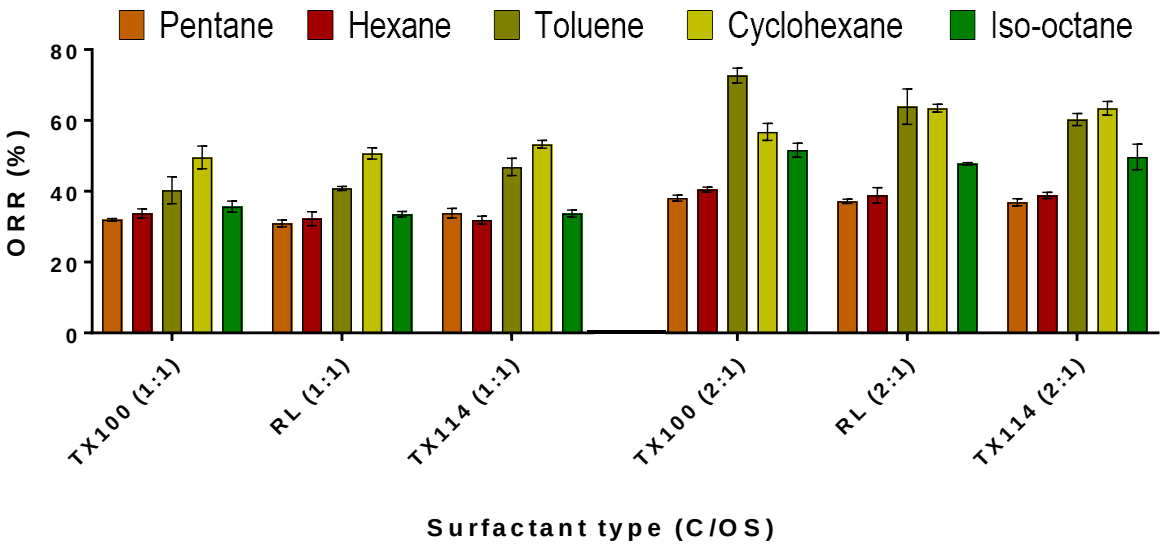

Figure 5.3. Oil recovery rate (ORR, %) with TX100, RL, TX114 at 2CMC and 1:1 S/OS for five co-solvents (pentane, hexane, toluene, cyclohexane, and isooctane) at two different C/OS ratios (1:1 and 2:1). The standard error of the mean (SEM) bars are shown (*n* = 3).

5.3.3. Effect of surfactant mixtures in oil recovery

Figure 5.4 shows the oil recovery values when all surfactants were combined in pairs. Each possible combination was evaluated. Since cyclohexane had comparable ORR values to toluene, the former was used as the co-solvent in the surfactant mixture experiment.

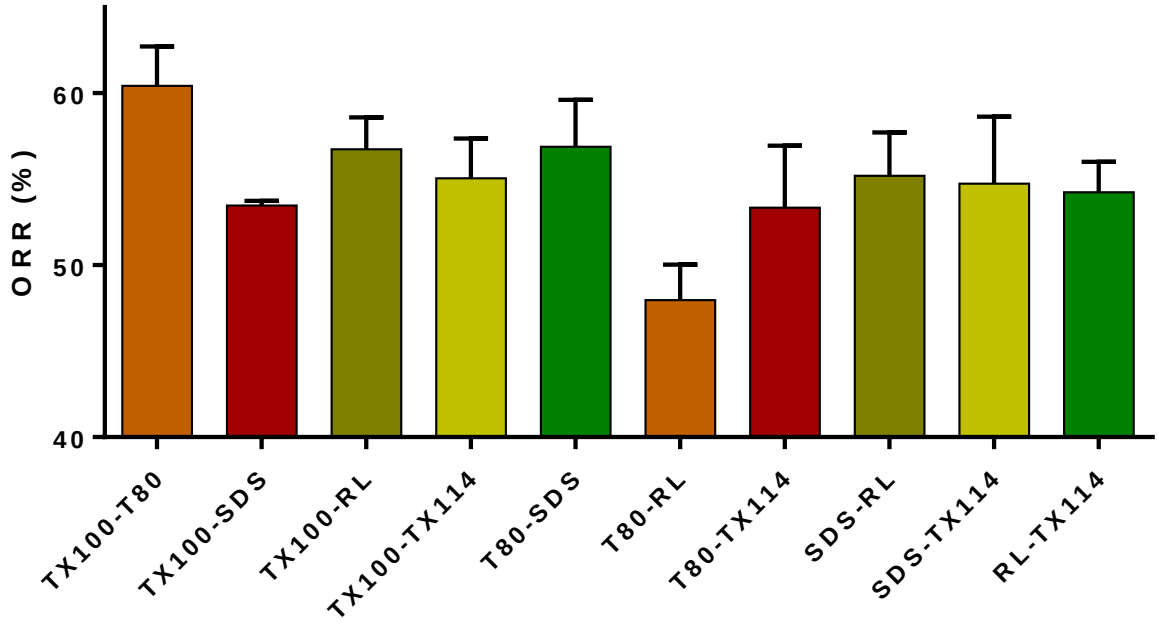

Figure 5.4. Oil recovery rate (ORR) values in a surfactant mixture 1:1 among all the surfactants used. Cyclohexane was used as the co-solvent (2:1 C/OS), and the surfactant mixture was added at a 1:1 S/OS ratio. The standard error of the mean (SEM) bars are shown (*n* = 3).

A one-way analysis of variance showed that there were no significant differences among the surfactant mixtures ($p = 0.183$). The highest ORR value was 60 (±4) % when TX100 and T80 were co-surfactants. When T80, RL and TX114 had TX100 as co-surfactant, the highest ORR values for each surfactant were 60 (±4) %, 57 (±3) %, 55 (±4) %, respectively. The lowest ORR value obtained in this experiment was 48 (± 4) % (T80-RL mixture) (Figure 5.4).

The highest ORR means from the surfactant mixture experiment were compared with the highest data from the co-solvent effect experiment with cyclohexane at 2:1 C/OS ratio. Only TX100, TX114 and RL were used in the co-solvent effect experiment, so these data were compared with the highest ORR mean values obtained for each of these surfactants in the surfactant mixture effect. There were no differences between both sets of data (co-solvent vs. surfactant mixture effects) when TX100 ($p = 0.329$), RL ($p = 0.077$) and TX114 ($p = 0.074$) were used.

5.4. Discussion

5.4.1. Co-solvent effect in the oil recovery

The highly significant effects of the co-solvent type and C/OS ratio factors can be visualised in Figure 5.3. The highest ORR values were obtained at the higher C/OS ratio (2:1) and also cyclohexane and toluene had almost two-fold increase in the ORR from 1:1 to 2:1 C/OS ratio in all three surfactants. This pattern is different compared with the other three co-solvents (pentane, hexane and isooctane), so in this case, the ORR did not change significantly between C/OS ratios (Figure 5.3).

The highest ORR value obtained in this study was about 73% when TX100 and toluene at 2:1 C/OS ratio were applied to the system. For the case of toluene, the highest ORR was 63% for both TX114 and RL at 2:1 C/OS ratio (Figure 5.3). These values are higher compared to other studies (Biceroglu, 1994; Avila-Chavez *et al.*, 2007; Zubaidy and Abouelnasr, 2010; Hu *et al.*, 2015). They reported ORR values that ranged from 30 to 40%. An exception is El Naggar et al. (2010) that reported an oil recovery rate of 76% using toluene. Since only co-solvents were used in these studies, the results obtained in this chapter could elucidate the important role of surfactants in the enhancement of the oil recovery.

In this study, low ORR values were obtained at a low C/OS ratio (1:1) because the amount of co-solvent was not sufficient to extract the oil that was recovered by the surfactant. There are several studies from the literature that support this premise. In fact, Kamal and Khan (2009) explained that the oil could saturate the co-solvent at low C/OS ratios which lead to low oil recovery values. On the contrary, at higher C/OS ratios, the solubility of oil in the co-solvent

can be enhanced, and therefore, ORR values can increase (Al-Zahrani and Putra, 2013). These results agreed with Hu et al. (2015) and Zubaidy and Abouelnasr (2010). For instance, the oil recovery using only MEK and LPG condensate increased with C/OS ratios from 1:1 to 4:1 (Zubaidy and Abouelnasr, 2010). This trend was also observed by Rincón et al. (2005a; 2005b) in their studies of base oil extraction from waste lubricating oil using MEK and 2-propanol. Also, Naggar et al. (2010) recovered more oil at high ratios of solvent to solid and semi-solid sludge. The added solvents included *n*-heptane, toluene, diethyl ether and methylene dichloride (El Naggar *et al.*, 2010).

As mentioned previously, the highest ORR values were obtained by cyclohexane and toluene in this experimental chapter. Moreover, there were no overall significant differences in the ORR between these two co-solvents ($p=0.62$). For instance, when TX114 was added, the ORR at 2:1 C/OS with toluene was 60% (±3) and with cyclohexane was 63% (±3). Toluene is commonly used by researchers in their oil recovery studies (Bock *et al.*, 1984; Jennings Jr and Abou-Sayed, 1994; El Naggar *et al.*, 2010; Atta and Elsaeed, 2011). Therefore, this co-solvent was the first choice in the preliminary OSW protocol performed on Chapter 4 (Section 4.2.3). Even though this OSW protocol proposed in this thesis is performed in a closed system, toluene is less benign to the environment and more harmful to human health compared to cyclohexane in an open system. Under this premise, cyclohexane can be a substitute of toluene in the next OSW experiments of this thesis. Young (2007a) reported that cyclohexane has a moderate overall toxicity (2 of 4) and according to the National Toxicology Program (NTP) at the 11th Annual Report on Carcinogens is not known to be carcinogenic (NTP, 2005). Hu et al. (2015) indicated that cyclohexane can be an appropriate solvent for oil recovery (41% ORR for 30 min of extraction at 4:1 C/OS) compared to dichloromethane, methyl ethyl ketone, and ethyl acetate. The oil recovery rate was approximately 30% for all these three solvents.

Cyclohexane has a high melting point (6.47 °C), so the solvent froze completely and prematurely in the OSW. On the contrary, when other co-solvents such as toluene were applied, the recovered oil and co-solvent layer were not frozen. Particularly, Hu et al. (2015) showed that the freeze/thaw treatment did not improve significantly ($p > 0.05$) the oil recovery in a solvent extraction using cyclohexane. These authors explained that the higher melting point of cyclohexane allows a premature freezing of the solvent before the water in the emulsion freezes. Specifically, since the molecular structure of cyclohexane is cyclic, the freezing step does not require very low temperatures. Therefore, this cyclic structure will fit easier into the crystal lattice whereas the fitting is more difficult in the lattice with an open structure of its

corresponding alkane (i.e. hexane). Then, lower freezing temperatures are required (Roberts and Caserio, 1977). Due to the selection of cyclohexane as the co-solvent on the next OSW experiments, the freeze/thaw step will be removed from the OSW protocol.

Table 5.1 shows some physicochemical properties of the co-solvents that can explain the differences in the performance of these solvents in the oil recovery. For instance, the differences in the molecular weight can be related with the performance of the co-solvents in the oil recovery. In fact, it has been a reported a positive relationship between the solvent molecular weight and oil recovery yields due to a decrease in the solubility difference between the solute and the solvent (Rincón *et al.*, 2005a). Toluene has a higher molecular weight (92.14 $g \cdot mol^{-1}$) compared to pentane (72.15 $g \cdot mol^{-1}$) and hexane (86.18 $g \cdot mol^{-1}$) that had low oil recoveries. Also, isooctane with the highest molecular weight (114.23 $g \cdot mol^{-1}$) had a higher oil recovery than pentane and hexane at a 2:1 C/OS ratio. However, the oil recovery of isooctane was lower than toluene and cyclohexane. The fact that isooctane had not obtained the highest oil recovery would suggest the influence of other physicochemical properties of the solvents such as the Hansen solubility parameter (iso-octane had the lowest HSP value, 14.3 $MPa^{½}$) and the contribution to hydrogen bonding (Burke, 1984). For instance, cyclohexane and toluene have the highest HSP values, and as mentioned before, these co-solvents had the highest ORR values. In the case of the hydrogen bonding, this is a parameter related to the solvation or dissolution event between the solvent and solute molecules (Spencer *et al.*, 1985). In this thesis, pentane, hexane, isooctane had the lowest oil recoveries that were less than 40%. This finding could be related to the fact that these co-solvents, which are aliphatic hydrocarbons, do not contribute to the hydrogen bonding compared to toluene that is considered to be a proton acceptor due to its aromatic nature (Burrell, 1973). Therefore, the dissolution of the solute (recovered oil) in the co-solvent is affected, so the oil recovery was lower compared to the ORR values of toluene and cyclohexane (Figure 5.3).

5.4.2. Co-solvent effect in the recovery of oil hydrocarbon fractions

The results showed that there was no an overall significant difference in the total EPH concentrations of the recovered oil ($p = 0.973$) among all three factors (co-solvent type, surfactant type, and C/OS ratio). This situation could be related to the fact that only one type of oil sludge sample (WSS) was used. Therefore, similar distribution in the oil fractions was obtained in all samples because the sludge came from the same source. However, Figure 5.2 showed that there were some highly significant differences among the co-solvents, as pentane, hexane, and isooctane had higher EPH concentrations in the C_{10}-C_{18} aliphatic fractions compared to cyclohexane and toluene. Particularly, this fraction had the highest percentage that ranged from 55% to 59%. Consequently, there were differences in the total EPH concentrations among the co-solvents (Figure 5.1). In fact, the co-solvent type was the only factor with highly significant effects ($p < 0.01$). The aromatic fraction had the lowest percentage among the analysed oil fractions (4 to 6%). In this study, PAHs had lower concentrations than aliphatic hydrocarbons. Also, Heidarzadeh et al. (2010) showed that PAHs were not detected in the analysed oil sludges. The sludges in their study came from oil/water separators, dissolved air flotation units, tank bottom sludge, and heat exchanger. In fact, it was mentioned in Chapter 2 (Section 2.3) that the percentage of the aliphatic fraction is generally higher than the proportion of the aromatic fraction in oil sludges (Shie *et al.*, 2004; Speight, 2006). In the case of the aliphatic portion, the light fractions (C_{10}-C_{18}) were higher than the heavy C_{19}-C_{36} aliphatic fractions. This difference was expected because the original EPH analysis of the sludge used in this experiment (WSS) reported a higher percentage of the C_{10}-C_{18} (60%) compared to a heavy C_{19}-C_{36} fraction (33%); the aromatic fraction (C_{11}-C_{22}) was 7% (Section 3.3.2.4; Figure 3.12).

Figure 5.1 and Figure 5.2 showed higher EPH concentrations at 1:1 C/OS. Moreover, the difference was not significant compared to the results obtained at 2:1 C/OS ($p = 0.139$). Also, Zubaidy and Abouelnasr (2010) reported that the concentrations of fuel oil were higher at low C/OS ratios. The authors proposed that high molecular oil hydrocarbons such as the asphaltenes in the crude oil are extracted at this low ratios because these heavier hydrocarbons have more affinity to the extracted fuel oil than the solvent itself. Therefore, this could contribute to the higher EPH concentrations at low C/OS ratio in this thesis.

n-hexane had one of the highest EPH concentrations in the recovered oil (Figure 5.1 and Figure 5.2). Also, Taiwo and Otolorin (2009) found that hexane recovered the highest concentration of hydrocarbons compared to xylene, kerosene, and ethyl acetate. In fact, *n*-pentane and *n*-hexane are used for TPH extraction from contaminated soils (ATSDR, 1999a; Reimers, 2001; Saari *et al.*, 2007; Okparanma and Mouazen, 2013; ASTM-D5765-16, 2016). For instance, Wu et al. (2011) used a solvent blend of hexane and pentane (4:1, v/v), and the TPH removal efficiency was around 95% after a 15-minutes treatment. However, it is not suitable to recover high amounts of oil and petroleum hydrocarbon compounds (Weisman, 1998), due to its simple linear molecular structure as pentane has. Therefore, this premise could contribute to the lower ORR values obtained for hexane in the oil sludge washing experiment (Figure 5.3).

In summary, the recovered oil had a high EPH concentration in the C_{10}-C_{36} fraction, so it can be used as a feedstock for fuel production (Wang *et al.*, 2003; Taiwo and Otolorin, 2009; Hu *et al.*, 2015), especially for the production of diesel oil (Kuriakose and Manjooran, 1994).

5.4.3. Surfactant mixtures effect

Since the objective of this experiment was to test only the effect of the surfactant type in the mixture, the ratio of the surfactant mixture was always the same (1:1). In fact, this ratio is considered to be a breakpoint between the antagonistic and synergistic effects of the surfactants mixed in the solution (See Section 2.11). Cyclohexane was used as the co-solvent because it was found that this solvent had comparable ORR values with toluene as mentioned in Section 5.3.1. Although Figure 5.4 showed that some mixtures had higher ORR values (TX100-T80, T80-SDS, TX100-RL), the values were not significantly higher ($p = 0.183$). Therefore, these results showed that the addition of these surfactant mixtures did not necessary improve the oil recovery for this type of oil sludge sample. Either that one surfactant is masking the effect of the other (antagonism) or that there is not effect at all, it is important to further test the CMC and surface activity (oil displacement test) of the mixture to assess any inter-surfactant effect.

In this study, TX100 and TX114 (non-ionic alcohol ethoxylate surfactants) had the highest oil recoveries in the surfactant mixtures (Figure 5.4). Sahni et al. (2010) mentioned that

alcohol ethoxylates (AEs) have an improved performance as co-surfactants, and they can increase the aqueous stability. T80 had high ORR (%) values when mixed with other surfactants (48% – 60%). In this case, the increasing ORR could be influenced by the sorbitan moiety found in the Tween surfactant, which gives extra stability of the mixed micelle (Chatterjee *et al.*, 2006). The sorbitan moiety of T80 belongs to the hydrophilic part of this surfactant where the polysorbate structure is found (Figure 5.5A). The sorbitan chemical structure is shown in Figure 5.5B for reference. The polysorbate structure in the hydrophilic part of the surfactant confers the stability of the micelle specifically in the hydrophilic heads inside the micelle core.

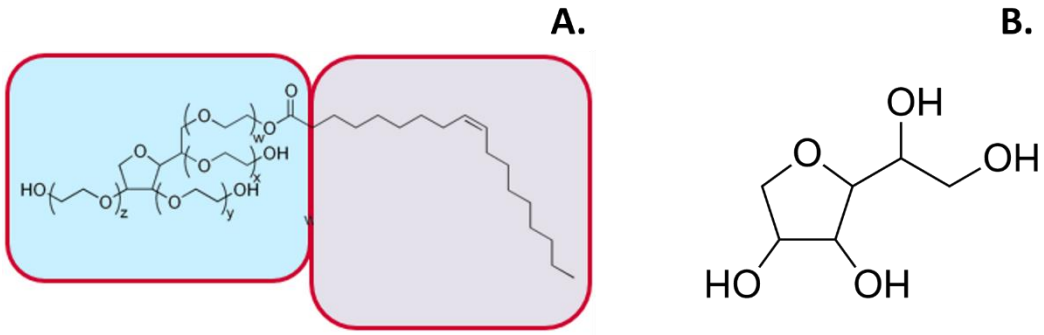

Figure 5.5. A) Chemical structure of T80 with its hydrophilic (blue) and hydrophobic (grey) parts. B) Sorbitan chemical structure. The depictions of the chemical structures are free licensed by Creative Commons.

The micellar stability given by the sorbitan moiety contributes to the reduced surface tension (Patist *et al.*, 1997), contributing to the synergistic effect related to the reduction of the CMC and enhancement of the oil recovery. Also, Patist et al. (1997) mentioned that the stability of mixed micelles increase if the surfactants of the mixtures have similar chain lengths. T80 had the longest chain (C_{64}) compared to TX100 (C_{34}), SDS (C_{12}), RL (C_{32}) and TX114 (C_{30}) (Table 3.1). It was expected that the oil recovery was higher with more stable micelles in the surfactants with similar chain lengths such as TX100 and TX114. However, the data had no clear patterns related to high recoveries using surfactants with similar chain lengths. This finding implies that other factors such as CMC and surface activity could be influencing the surfactant mixture, so it is necessary to study these factors in the future as mentioned before.

Even though the sorbitan moiety can benefit the ORR by giving stability to the micelle, the lowest oil recovery of this study [48% (±4)] was obtained with the mixture of T80 and RL (Figure 5.5). This result can be explained by a negative impact of steric effects or molecular influence between the molecules of these surfactants (Zhou and Rosen, 2003). In fact, T80 is the surfactant with the highest molecular weight value (1309.68 $g \cdot mol^{-1}$) among all of the surfactants used in this study. In fact, this molecular complexity is related to its highy branched hydrophilic head group (Figure 5.5A). Furthermore, the molecular complexity of the hydrophobic can have also steric effects in the surfactants. For instance, Figure 5.6 shows the degree of chain branching in the hydrophobic part for the surfactants used in this thesis. The high complexity in these hydrophobic groups of each surfactant could enhance the antagonistic effect of the mixture, decreasing the ORR value. RL molecule has the most complex hydrophobic tail group compared with the other surfactants as this group is branched. Conversely, SDS has the least complex hydrophobic part with a linear chain (Figure 5.6).

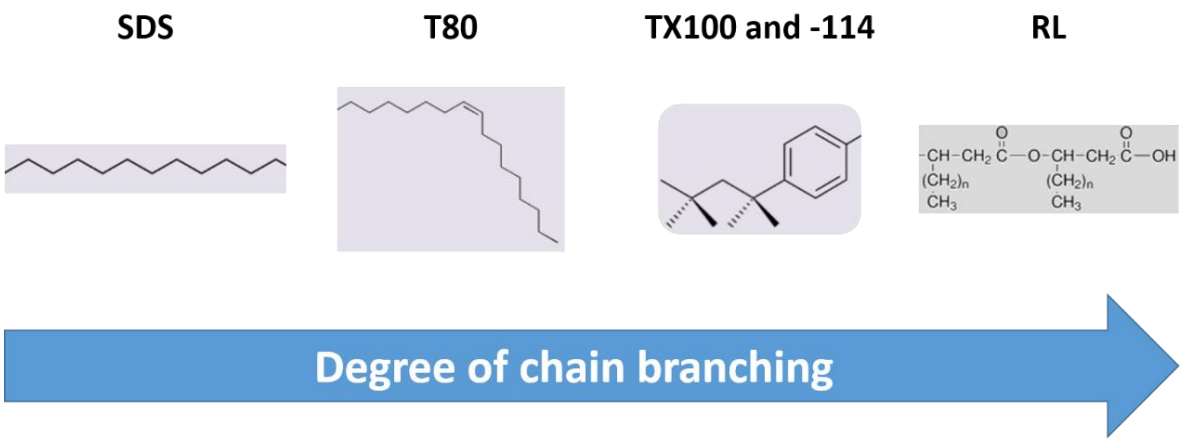

Figure 5.6. Degree of branching in the hydrophobic part of all surfactants used in this study. All chemical structures depictions are free licensed by Creative Commons. Specifically, the depictions for TX- and RL were taken from Hoffmeier (2007) and Sigma-Aldrich (2015), respectively.

The surfactant mixture effect data was compared with the highest ORR values obtained in the co-solvent effect data at the 2:1 C/OS ratio. In this case, there was no significant improvement in the oil recovery using surfactant mixtures with only one type of sludge sample from an oil-water separator.

5.5. Conclusions

This study found that the highest ORR values were obtained at the higher C/OS ratio (2:1). Notably, these ORR values obtained in this study (about 75%) were higher compared to other studies (30 – 40%). Since these reports only used co-solvents in the process, the results from this thesis can show the key role of surfactants in the oil recovery. Also, it was found a differential performance of the co-solvents in the oil recovery. Cyclohexane and toluene had almost two-fold increase in the ORR between the evaluated C/OS ratios. However, the ORR did not change significantly between the C/OS ratios when pentane, hexane and isooctane were used.

The ORR using cyclohexane and toluene was enhanced by higher C/OS ratios due to a probable effect of the high solubility of the extracted oil into the solvent. Moreover, cyclohexane had no significant differences in the oil recovery compared to toluene. This solvent is less hazardous to the environment than toluene (Table 5.1), so cyclohexane can be an alternative solvent to toluene. In fact, this solvent will be used in further experiments of this thesis.

This chapter reported that the aliphatic fraction had higher EPH concentrations compared to the aromatic fractions in all the samples analysed. Particularly, the EPH concentration was higher for the C_{10}-C_{18} aliphatic fraction. This finding indicates that the recovered oil from this sludge can be used as a feedstock for light grade of fuel oils such as diesel (Giles, 2010). Hexane was able to extract the highest EPH concentrations in this study. In fact, this is the most used solvent for TPH extractions. However, this solvent had low ORR values compared to cyclohexane and toluene because hexane cannot recover high quantities of oil due to its simple linear molecular structure.

Even though there were no significant differences in the total EPH concentrations of the recovered oil among the co-solvent and surfactant type factors and the C/OS ratio, there were highly significant differences among the co-solvents. In fact, there were differences in the concentrations of oil fractions, specifically in the C_{10}-C_{18} aliphatic fraction. Moreover, higher EPH concentrations were found at the 1:1 C/OS ratio. This finding could be due to a higher affinity of heavier hydrocarbons that was favoured by a lower amount of co-solvent.

A modification of the OSW protocol (Section 4.2.3) was done after it was decided that cyclohexane was the preferred co-solvent for the next OSW experiments in other sludges. Since cyclohexane has a high melting point (6.47 °C), the top layer of recovered oil and this co-solvent was frozen completely and prematurely before the water did in the OSW process. In fact, this event could affect the performance of cyclohexane in the oil recovery. Therefore, the freeze/thaw step is not necessary, and consequently, it will be removed from the OSW protocol in the next chapter of the assessment of the oil recovery from different sludges.

The differential ORR values among the co-solvents could be based on their physicochemical properties. For instance, the HSP values of the co-solvents could explain that the highest ORR values were obtained for cyclohexane and toluene as these co-solvents had the highest HSP values. This high solubility of both co-solvents and the higher contribution to hydrogen bonding could imply a better performance in the oil recovery. Moreover, when comparing the molecular weight of the co-solvents, toluene has a higher molecular weight compared to other solvents such as pentane and hexane. This fact could explain in part why toluene had higher recoveries which could be related to a decrease in the solubility difference between the solute and the solvent. However, isooctane had the highest molecular weight but lower ORR, which implies that the HSP was more suitable to explain the differences among ORR values in the co-solvents.

When comparing the ORR values of all the possible surfactant mixtures combinations, there were no significant differences among these combinations. Therefore, there was no enhancement in the oil recovery for this type of oil sludge sample. However, some surfactants such as TX100 and TX114 had the highest oil recovery values which can be explained by the AE compounds present in their chemical structure. Also, the high ORR values found when T80 was in the mixture could be due to its chemical structure. In this case, the sorbitan moiety present in T80 could contribute to an extra stability of the mixed micelle. Also, the molecular complexity and steric effects of the hydrophobic groups could be related witht the low

recoveries as it was found for RL. Since the oil recovery did not improve with the surfactant mixture compared with the co-solvent data, the OSW for further experiments with the different sludges will use only one surfactant. Indeed, the surfactant mixture effect can be different for the other type of sludges. However, this decision of using only one surfactant was based on the fact that having two surfactants will be an extra factor in the experimental design which implies a higher number of experimental runs.

Chapter 6 - Oil sludge washing of different types of oil sludges and the toxicity of the residuals

6.1. Introduction

Previous experiments of this thesis have focused on the oil recovery from one type of oil sludge (WSS from an oil-water separator). However, it is necessary to analyse the effect of OSW in the oil recovery from other types of oil sludges to develop a robust methodology. In fact, most of the oil sludge treatment studies, including oil recovery, have been focused on oil sludges from the bottom of storage tanks (Hu *et al.*, 2013). However, oil sludges can also be generated by other sources such as desalinators, oil/water separators, industrial wastewater, and from the washing of pipes in the petroleum refinery facilities (da Silva *et al.*, 2012). For these reasons, four oil sludges from different sources were chosen in this study. These sludges included an oil drilling sludge (ODS), a waste engine oil sludge obtained from both gravitational settling in a storage tank (STS) and centrifugation (RS), and a sludge containing a high amount of crude oil (NSC) (See Chapter 3: Section 3.3.2).

This thesis has used alternative experimental designs to cope with a large number of experimental runs. For instance, the Taguchi orthogonal arrays applied in the experimental design on Chapter 4 facilitated the optimisation of OSW parameters in the oil recovery at early stages of experimentation. This chapter was not the exception, and another type of experimental design (D-optimal) was applied due to its convenience with the experimental requirements, as the factors had mixed number of levels.

One of the conclusions from Chapter 5 was that cyclohexane had oil recovery values similar to toluene. Even though the OSW method proposed in this thesis is in a closed system, the preference of cyclohexane over toluene was based on the fact that this solvent is less hazardous when exposed to both the environment and human health compared to toluene (Henderson *et al.*, 2011). Therefore, Table 5.1 shows that cyclohexane has a lower impact in the environment and human health, compared to toluene. Consequently, cyclohexane was used as the co-solvent in the present chapter.

After oil recovery, there are some residuals left from the oil sludge washing (OSW) process. These OSW residuals are sediments and water from the sludge and the surfactant solution. This waste can have remnants of oil and heavy metals (Hu *et al.*, 2013). Therefore, it

is necessary to test the remaining degree of contamination of oil with inorganic compounds such as potentially toxic elements (PTEs) and to check the toxicity of the OSW residuals. These assessments are necessary to establish further waste treatment processes. If the residuals still contain a burden of oil and PTE co-contamination, there is a need to assess the ecotoxicity associated with this contamination to decide if bio-remedial methods that rely on the activity of organisms such as microorganisms (landfarming) and plants (rhizoremediation) are appropriate for subsequent treatment of the residual oil hydrocarbons. Heavy metal hyperaccumulating plant species can be used to treat PTEs (McCutcheon and Schnoor, 2003). For instance, Bhandari et al. (1994) mentioned the importance of performing pretreatment techniques (e.g. soil washing) of petroleum contaminated soils to decrease the contamination levels. Then, bioremediation techniques can be applied due to the lower toxicity to microorganisms. Also, as mentioned before, the plants used in the phytoremediation of OSW residuals amended to the soil can also have a beneficial economic benefit with the biodiesel production if phytoremediator species such as soybeans are used. Indeed, the toxicity tests can elucidate any potential detrimental effect on the plants and microorganisms before applying the further treatment techniques of the residuals. In addition, Wilke et al. (2008) stated that the ecotoxicological tests are a complement to the chemical analyses because these tests are sensitive to the bioavailable fraction of the contaminant.

The first objective of this chapter was to assess the effect of the OSW parameters (surfactant type and concentration, and S/OS ratio) upon the oil recovery from different types of oil sludges. The second objective was to test the effect of these residuals upon soil microorganisms by undertaking the dehydrogenase activity (DHA) test, and upon plants by assessing the effect of these residuals on the germination of ryegrass. The DHA test measures the aerobic microbial oxidation in soil by evaluating the activity of dehydrogenases. These enzymes are present in the electron transport chain that leads to oxygen as the final acceptor of electrons (Shaw and Burns, 2006). The DHA test is a sensible marker of toxicity for the soil microbiota as it has been reported that petroleum hydrocarbons can ameliorate the activity of soil microbial enzymes such as dehydrogenase and invertase (Suleimanov *et al.*, 2005).

6.2. Materials and Methods

6.2.1. Oil sludges

Four oil sludges (analysed previously in Chapter 3) were used in this study. One oil drilling sludge (ODS) with a total EPH concentration of 6,000 (±145) ppm, and another sludge from an oil refinery (NSC) with 68,000 (±6,000) ppm. Also, STS and RS (waste engine oil sludges) were analysed with total EPH concentrations of 1,500 (±500) and 950 (±400) ppm, respectively. The former was obtained after gravitational settling and the latter by centrifugation (See Section 3.3.2 for more information of the characterisation of the oil sludges).

6.2.2. Experimental design for the effect of OSW parameters in the oil recovery

About 1,500 experimental runs are needed if a full factorial design is applied to test the effect of surfactant concentration and surfactant to oil sludge (S/OS) ratio. This design includes the four types of oil sludges mentioned before, five types and five concentrations of surfactants, and 5 S/OS ratios with three replicates. Therefore, there is a need to establish the most convenient and efficient experimental design to reduce the number of experimental runs.

Two-stage experiments were done to simplify the design. First, the test of the effect of S/OS ratio was tested, and after the determination of the surfactant concentration effect. For testing the effect of the S/OS ratio, the lowest and highest ratios used in this thesis, 1:1 and 5:1 S/OS ratios, were analysed (Table 6.1). Each surfactant was prepared according to the CMC concentrations with the maximum oil recovery obtained in the OSW parameters experiment with the WSS sample on Chapter 4 (Figure 4.4). Cyclohexane was applied at a 1:1 ratio to the sludge. The total number of experimental runs, including three replicates, was 120. A three-way analysis of variance was performed on the ORR data with effects for the type of sludge and surfactant, and S/OS ratio; a *post-hoc* Tukey's test was done to reveal differences among the treatments.

Table 6.1. Parameters evaluated in the factorial design of the S/OS ratio effect.

Sludge	Surfactant*	S/OS ratio
ODS	TX100 (1CMC)	1:1
STS	T80 (4CMC)	5:1
RS	RL (2CMC)	
NSC	TX114 (2CMC)	
	SDS (0.5CMC)	

***** The concentrations used for each surfactant were based on the concentrations that had the highest ORR in the preliminary study on Chapter 4 (Figure 4.4).

Once the optimal S/OS ratio in the oil recovery per sludge was known, the second stage of this experiment was done considering the following factors: four types of oil sludge, five types of surfactant, and four surfactants concentrations (0.5 CMC, 1CMC, 2CMC, 5CMC). Since three factors with mixed five and four levels were considered at this second stage, a factorial design had a total of 240 experimental runs including three replicates. Therefore, a D-optimal design, a non-traditional experimental design, was chosen because it can analyse multi-level factors by using a computer algorithm and a model; no orthogonal array is needed as in the Taguchi design (NIST, 2013). Fractional factorial designs such as Plackett-Burman cannot be used because these designs only work for two-level factors. Moreover, a response surface is not suitable because all the factors have to be numeric, and the only factors with numeric levels in this study are the surfactant concentration and the S/OS ratio.

Since a Taguchi design is applied at an early stage of experimentation, the D-optimal experimental design was chosen because the data from the WSS sludge (Chapters 4 and 5) can be added as an input to the model. The D-optimal design was done using the software JMP®, Version 12.1. (SAS Institute Inc., Cary, NC, 1989-2007), and it is based on the optimality criterion which minimises the generalised variance of the parameter estimates in the pre-specified model (National Institute of Standards and Technology (NIST), 2013). Therefore, the uncertainty in the predicted response decreases (de Aguiar *et al.*, 1995). By having this pre-specified model, precise estimates of the coefficients are considered by the optimality criterion (JMP, 2013). The software finds the best design among all the possible options by selecting the design with the highest D-efficiency (%). This value is based on the generalised variance. For example, a full factorial design will have a D-efficiency in the design of 100% because all possible experimental runs are considered (NIST, 2013). The D-optimal method is a balanced

design which has an equal number of runs for each level of a factor (Eriksson *et al.*, 2008). Therefore, each of the four levels for both the type of sludge and surfactant concentration factors appeared 15 times and 12 times per level, respectively, for each of the five types of surfactant. In this case, the balanced design is based on the type of surfactant (qualitative factor), so each surfactant will be paired 15 times with the levels of the type of sludge and 12 times with the corresponding levels of the surfactant concentration factor. The final number of experimental runs obtained with this model was 60, and this was done in triplicate (a total of 180 experimental runs). The model included a blocking factor for days because there were highly significant differences among the Taguchi experimental design blocks in the preliminary OSW study, where one block corresponded to a replicate per day (See Chapter 4). Then, this experiment was done in two days in which 30 runs were randomly assigned per day in triplicate using Research Randomizer (Urbaniak and Plous, 2013). A three-way analysis of variance was performed on the ORR data with effects for the type of sludge and surfactant, and surfactant concentration. A *post-hoc* Tukey's test ($\alpha = 0.05$) was also done.

Additionally, a control with no surfactant solution, ultrapure water only (18.2 MΩ·cm), was tested. A paired t-test ($\alpha = 0.05$) evaluated if the mean of ORR using surfactants is higher than the mean of ORR with no surfactant solution.

The oil sludge washing process followed the procedure mentioned in Chapter 4 (Section 4.2.3) using cyclohexane as the co-solvent. Since the melting point of cyclohexane is 6.47°C, the freeze/thaw step was not done. The EPH extraction (Section 3.2.2.4), SPE clean-up with separation of aliphatic and aromatic compounds (Section 3.2.2.5), and EPH analysis (Section 3.2.2.6) with the MADEP method (2004) of the samples were described in Chapter 3. All statistical analyses used Minitab 17.3.1 (Minitab Inc.), and graphs were created using GraphPad Prism 7.01 (GraphPad Software, Inc.).

6.2.3. Toxicity tests of the OSW residuals

6.2.3.1. Sample preparation for the toxicity tests

The DHA test was performed first due to its utility in terms of time, sample amount and setup. The outcome of the DHA test was used to establish a range of concentrations of OSW residuals in the soil which were suitable for the ryegrass germination test, as this test has more complexity in terms of material and methodology. First, all sludges (ODS, RS, STS, and NSC) and all OSW residuals were analysed with the DHA to have an overall assessment of the toxicity and to determine the incubation time for the DHA test. The toxicity experiments (DHA and germination test) involved soil amended with varying concentrations of the OSW residuals (Table 6.2).

Table 6.2. Percentages of different types of OSW residuals amended in the soil for the toxicity tests.

Toxicity Tests	**OSW residuals (%) in soil**				
	1%	*5%*	*10%*	*25%*	*50%*
Dehydrogenase activity	All sludges (TX100, SDS)	All sludges (TX100, SDS)	STS (TX100, RL, SDS)	STS (TX100, RL, SDS)	STS (TX100, RL, SDS)
Seed Germination	ODS, STS (TX100)	ODS, STS (TX100)	ODS, STS (TX100)		

All surfactants used to prepare the OSW residuals were applied at the highest concentration evaluated in this thesis (5CMC). OSW residuals concentrations in soil were based on the values proposed by Singh and Agrawal (2007) and Mazen et al. (2010) in their sewage sludge addition to soil study. The rationale behind the selection of the surfactants and sludges in the residuals is explained in the results (Section 6.3.5). These choices were based on the results of the first DHA test which assessed the OSW residuals with all possible combinations of surfactants and sludges.

The soil (20-cm depth) used in the dehydrogenase activity and germination tests was collected from Sonning, Berkshire, UK (SU 762 754; GB grid). For the dehydrogenase test, fresh field moist soil was sieved (2.0 mm) and stored at 4°C before the test. Soil used for the germination test was dried in an oven for four days at 40°C. Then, it was put through a 2.0 mm-sieve and ground (Greene *et al.*, 1989). The 2.0 mm sieved soil was thoroughly mixed with the OSW residuals using a Stuart roller mixer SRT9D (Bibby Scientific Ltd.) for 60 minutes at 60 rpm before use. A stock of each concentration was taken and then divided into subsamples for both toxicity tests.

6.2.3.2. Dehydrogenase activity (DHA) test

This test uses the water-soluble iodonitrotetrazolium chloride (INT) as an artificial electron acceptor, which can be biologically reduced by the dehydrogenase activity in the aerobic microbial oxidation (Shaw and Burns, 2006). This reduction can be measured by the change in colour from yellow to purple, which is the reduced water-insoluble compound, iodonitrotetrazolium formazan (INTF) (Shaw and Burns, 2006). The DHA test was originally proposed by Benefield et al. (1977). The method used in this study was adapted by Shaw and Burns (2006) from Trevors (1984a) and (1984b), and von Mersi and Schinner (1991). All the lab material used for the DHA test was autoclaved. One (1) g of the OSW residual-spiked soil or sludge and 4 ml of 0.2 % (v/w) INT (Manchester Organics) were added into sterile McCartney bottles (28 ml). The INT was dissolved for four hours with agitation in ultrapure water (18.2 Ω·m). Since the INT media is heat-sensitive, it could not be sterilised with an autoclave. Therefore, the solution was sterilised through a 0.2 µm filter. For reference, the average size of a bacterial cell is about 2.0 to 5.0 µm in length and 0.5 to 1.0 µm in diameter (Srivastava and Srivastava, 2003). Samples were incubated at 25°C in the dark. A previous trial gave the most appropriate incubation time which was 24 hours (See Results, Section 6.3.5). This determination is crucial to know the minimum incubation time in which the INTF can be detected. After, the samples were extracted with 10 ml of N,N-dimethyl formamide:ethanol (1:1, v/v) solution and incubated at 25°C for 1 hour in the dark with constant agitation (200 rpm). Following the extraction period, the extractant and sample mixture (2 ml) were transferred to 2 ml microcentrifuge tubes. The tubes were centrifuged using a relative centrifugal force (RCF) of 11,600 x g for 5 min. Samples were analysed using a

spectrophotometer at 464 nm (Cecil Digital Ultraviolet Spectrophotometer, Series 2, CE 292). A calibration curve (0 – 25 µg·ml-1) was prepared using a mixture of extractant:ultrapure water (18.2 Ω·m) to dissolve each concentration of INTF standard (Sigma-Aldrich).

The absorbance for each sample replicate was corrected by subtracting the mean of the biotic control (sample with water instead of the INT). This biotic control with water accounts for the red colour that is in the soil produced during the incubation, and that it is not related to INTF. This corrected biotic sample was subtracted from the mean of the abiotic control. Since the sludge and OSW residuals could not be sterilised, a sample incubated at zero hours was assumed to be the sterile or abiotic control. This control checks for reduction of INT that is not related to biological activity, and assumes that any chemical reaction bringing about the abiotic reduction of INT is instantaneous. Therefore, it can be measured after 0 h incubation. The real INTF concentration was obtained from the calibration curve equation and by multiplying by 14 (total volume in ml of INT and extractant added for each sample). This value was the measurement of the dehydrogenase activity (DHA) reported in the results. A two-way analysis of variance was performed on the data with effects of OSW residuals and surfactant type.

6.2.3.3. Seed germination toxicity test

The seed germination toxicity test was based on the standard procedure from the American Society for Testing and Materials (ASTM-E1963-09, 2014) and a protocol suggested by Greene et al. (1989). Ryegrass seeds (*Lolium perenne*) were obtained from Emorsgate Seeds. Plastic Petri dishes (Sigma-Aldrich), 15 cm wide by 1.5 cm high, were used as the test chambers, and 100 g of the homogenised contaminated soil were added (Table 6.2). Seeds (25) of equal size were sowed in a pattern of five columns by five rows. The seeds were approximately at least 0.5 inches from the edge of the dish. The seeds were pressed into the soil by using the bottom of a clean beaker. The water holding capacity of the system was adjusted to 85% with ultrapure water (18.2 MΩ·cm). Then, a cover of sand (90 g) was added on the top of the soil. A ruler was used to level the sand, and the Petri dish was covered with a lid. The location of each Petri dish in the greenhouse was randomised using Research Randomizer (Urbaniak and Plous, 2013). The Petri dishes were exposed to the natural daily cycle (13 and 11 hours of light and dark, respectively). The lids of the Petri dishes were opened

once daily for aeration, and each test chamber was watered accordingly to maintain the water holding capacity of each dish.

The pH of the contaminated soil samples was analysed to ensure that there were no pH-related toxic effects. Therefore, the pH was measured before and after the germination experiment as suggested by the Ministry of Agriculture, Fisheries and Food method (MAFF, 1986). Sample (10 g) and 25 ml of ultrapure water (18.2 MΩ·cm) were added into a 50 ml centrifuge tube. The sample was agitated in an end-over-end shaker at 20-30 rpm for 15 minutes. The pH was measured with a FiveEasy™ pH meter (Mettler Toledo). The germination rate (Equation 6.1) was determined by counting emerging seedlings above the sand cover (Besalatpour *et al.*, 2008).

$$Germination\ rate = \frac{N°\ of\ germinated\ seeds}{(N°\ of\ planted\ seeds = 25)} \times 100\%$$

Equation 6.1. Germination rate (%).

The temperature and relative humidity were recorded every hour with an electronic data logger. The data was extracted and processed with the software RH and Temp Datalogger v. 1.5.

A positive germination control with Kettering loam soil and two reference toxicants, diesel germination and boric acid (H_3BO_3) negative germination controls were used. The organic reference toxicant diesel was added to the 2.0 mm sieved soil to give a final concentration of 50,000 ppm (Adam and Duncan, 2002). The boric acid was added to the sieved soil as a 5% (w/v) solution in ultrapure water (18.2 MΩ·cm). Due to the inorganic nature of this negative control, the effect of volatilisation and photodegradation of the petroleum hydrocarbons present in the residuals could be evaluated (Stephenson *et al.*, 1997), as the diesel is susceptible to these phenomena. Also, it was included a control with 5% of the surfactant solution in the soil. A paired t-test ($\alpha = 0.05$) was used to assess the mean differences between the germination rates of OSW residual-treated and non-treated soils.

6.3. Results

6.3.1. Oil recovery from different oil sludges considering the effect of the S/OS ratio

The type of surfactant and the S/OS ratio effects on the oil recovery were dependent on the type of the sludge (Figure 6.1). A three-way ANOVA revealed an overall highly significant effect of the type of sludge and surfactant, and the S/OS ratio factors on the ORR ($p < 0.01$). Indeed, there was an effect of S/OS ratio and type of sludge in the oil recovery as both factors had p-values less than 0.01. However, the only non-significant factor was the type of surfactant ($p = 0.651$). A *post-hoc* analysis ($\alpha = 0.05$; Tukey's test) showed that each type of sludge was significantly different to the other, except for STS and RS that were not different. This similarity was expected as both sludges came from a similar source (i.e. waste engine oil sludge).

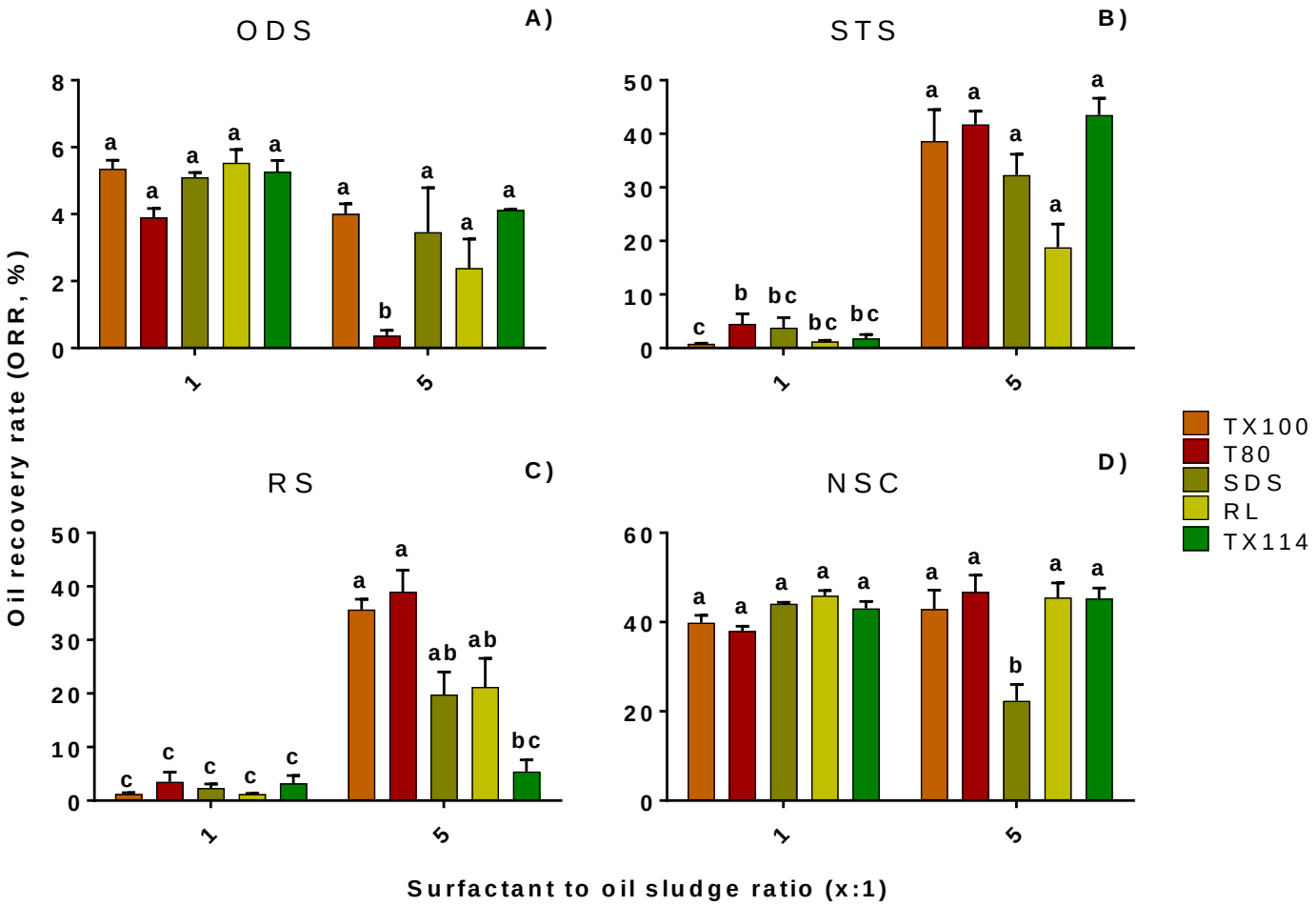

Figure 6.1. Oil recovery rate (ORR, %) from all oil sludges and surfactants at two S/OS ratios (1:1 and 5:1). Cyclohexane was added at 1:1 C/OS ratio. ORR (%) mean values with the same letter are not significantly different; the comparison of S/OS ratios with surfactants per oil sludge was analysed (p > 0.05; Tukey's test). The standard error of the mean (SEM) bars are shown (*n* = 3).

ODS (Figure 6.1A) had significantly higher oil recoveries at 1:1 S/OS ratios ($p < 0.01$). A *post-hoc* test ($\alpha = 0.05$) evidenced that T80 at 5:1 S/OS ratio had a significantly lower oil recovery rate from ODS (0.37% ± 0.28) compared to the other surfactants (2% to 5% ORR). The Tukey's test ($\alpha = 0.05$) showed that SDS was significantly different due to a low ORR compared to the others surfactants that had no differences (Figure 6.1A). STS (Figure 6.1B) and RS (Figure 6.1C) had higher ORR values at 5:1 S/OS ($p < 0.01$). STS and RS had a significantly higher ORR with the addition of T80 compared to the other surfactants ($p = 0.007$ and $p = 0.053$, respectively). The oil recovery from NSC was not significantly different ($p = 0.095$) between 1:1 and 5:1 S/OS ratios (Figure 6.1D), except for SDS at 5:1. This value was significantly lower, 22% (± 6), compared to the other surfactants (ORR ranged from 38% to 47%). In general, TX100 and T80 were the surfactants with the highest ORR values among all sludges.

The best S/OS ratios obtained in Figure 6.1 were used to establish the optimal surfactant concentrations in the OSW for all the sludges. The S/OS ratio selected for ODS was 1:1 and for STS, RS and NSC were 5:1. Despite that there were no differences between both ratios for NSC, the S/OS ratio chosen was 5:1. This ratio was selected because it has been reported higher recoveries at higher ratios as mentioned in Chapter 4 (Peng *et al.*, 2011; Wu *et al.*, 2012). The model for the experimental design with the highest D-efficiency (89.91%) and lowest average variance of the prediction (0.94) was selected.

6.3.2. Surfactant concentration and its effect on the oil recovery from different sludges

The effect of surfactant concentrations in the OSW of the oil sludges is shown in Figure 6.2. Since the surfactants perform a crucial role in the OSW, as mentioned before in previous chapters of this thesis, the ORR data from all sludges is presented per surfactant.

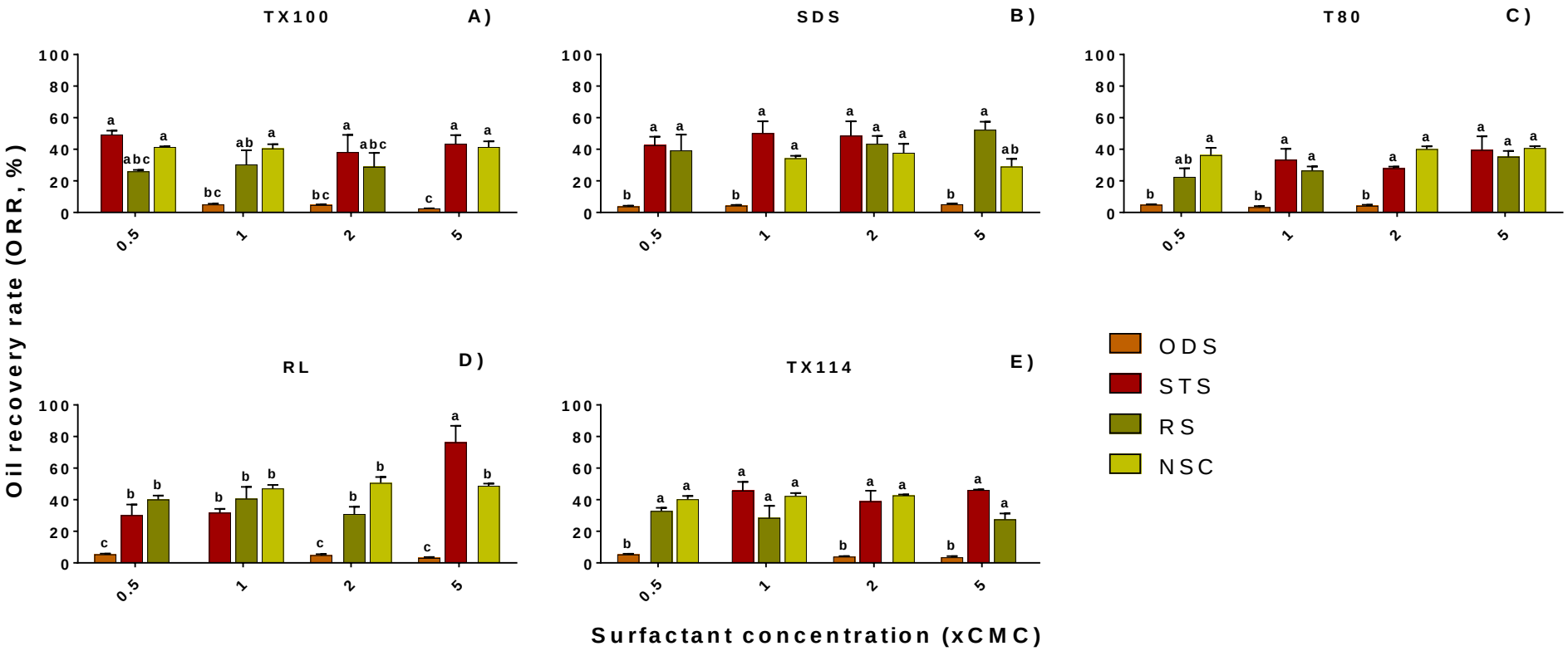

Figure 6.2. Oil recovery rate (ORR, %) from all oil sludges and surfactants at different surfactant concentrations. S/OS ratios were fixed for each sludge, and these ratios were selected from Figure 6.1. Cyclohexane was added at 1:1 C/OS ratio. ORR (%) mean values with the same letter are not significantly different; the comparison of surfactant concentrations with oil sludges per surfactant was analysed ($p > 0.05$; Tukey's test). The standard error of the mean (SEM) bars are shown ($n = 3$).

A one-way ANOVA revealed that there were differences in the sludge ($p < 0.01$) and surfactant type ($p = 0.009$) factors, but there was no effect of the surfactant concentration factor in the oil recovery ($p = 0.745$). Consequently, there were no differences in the two-way surfactant type and concentration interaction ($p = 0.158$). A *post-hoc* Tukey test ($\alpha = 0.05$) elucidated the differences among the oil sludges per surfactant. Contrary to the previous experiments in Chapter 4 and 5, there were no differences between the two days (blocking factor) of the surfactant concentration effect experiment ($p = 0.243$). Overall, the highest ORR values per surfactant were the following:

- STS: 76% (± 18) with RL (5CMC)
- RS: 52% (± 9) with SDS (5CMC)
- NSC: 51% (± 6) with RL (2CMC)
- ODS: 5% (± 0.87) and 5% (± 0.77) with RL and TX114 at 0.5CMC, respectively.

The layers obtained after the OSW were also visually different in all sludges (Figure 6.3). It was observed more sediment from the ODS sample (Figure 6.3A) as expected since the solid content of this sludge was 86% (±0.11). The lowest amount of sediment material was observed from NSC; its solid content was 1% (±0.07) (See Chapter 3, Section 3.3.2.2 for the solid content data). When RL was used in the washing of NSC, the top oil layer was clean with no visual mixing with sediment (Figure 6.3D). It has to be clarified that since the NSC sample was limited (Chapter 3), less amount of sample was used compared to the other samples. However, the same S/OS ratios in NSC were kept as in the other sludges. RS and STS had a similar appearance in the OSW layers due to their shared source of origin. The oil recovery from these sludges was the most difficult to perform since it seems that the oil had a strong O/W emulsion, as some water and sediments were extracted in the oil phase. For example, this situation was observed in RS with TX100 at 2CMC and TX114 at 0.5CMC (Figure 6.3C) and STS (TX114 at 2CMC and 5CMC, RL 1CMC,). Therefore, the extracted top oil phase was left stand to allow a further gravitational separation of remnant water and sediments. On the contrary, when SDS (e.g. 2CMC) was added to extract oil from RS, the oil layer was easily separated, and no further gravitational separation was necessary. Also, when RL at 0.5CMC and 2CMC were added into ODS sludge, the oily top layer was easier to separate. However, when SDS at 5CMC was applied to ODS, the recovered oil had some sediment. Moreover, SDS affected negatively the OSW from NSC (the oil extracted had some sediment) whereas the addition of RL (Figure

6.3D) and TX114 to NSC contributed to a simple extraction of the top oil layer. Similarly, the demulsification role of RL (Long *et al.*, 2013) in STS and RS allowed removing water from the top oil layer. In fact, this top layer appeared highly viscous with no visible water phase.

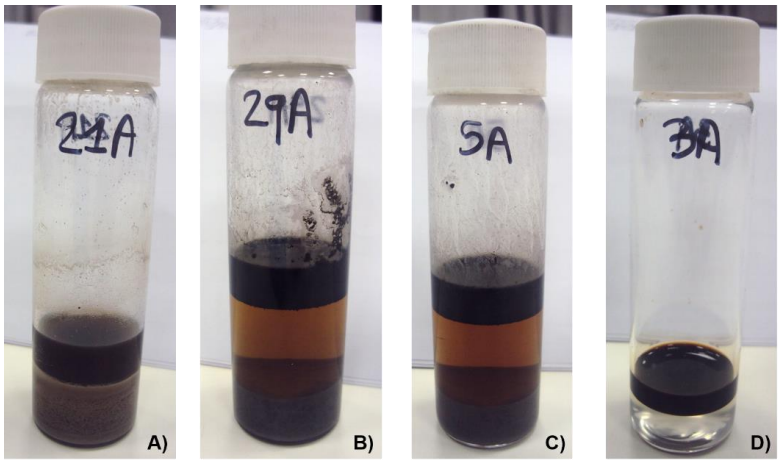

Figure 6.3. The final stage of the OSW with the three layers from the analysed sludges: Oil and cyclohexane (top layer), water and surfactant (middle layer), sediment (bottom layer). A) ODS with T80 at 0.5CMC (1:1 S/OS). B) STS with TX100 at 2CMC. C) RS with TX114 at 0.5 CMC. D) NSC with RL at 1CMC. The S/OS ratio in B, C, and D was 5:1.

Table 6.3 showed the ORR with no surfactant solution (only water) and cyclohexane (1:1 C/OS) from all the oil sludges used in this study. These results were compared with the highest ORR values obtained in the surfactant concentration effect experiment. Also, the WSS sludge used in the previous OSW experiments (Chapter 4 and 5) was included for comparison. A paired t-test ($\alpha = 0.05$) evaluated if the mean of ORR with surfactants was higher than the mean with no surfactant treatment. Overall, the use of the surfactant did not have a significant difference in the oil recovery for ODS, STS, RS, and NSC (Table 6.3). However, in the case of WSS, the mean ORR of the surfactant-treated OSW was significantly higher ($p < 0.01$) than the control with no surfactant. In addition, the oil phase obtained from the OSW of all sludges had a facile separation similar to RL when only water was used in the OSW. Another OSW

assay without the co-solvent showed no clear separation of layers with and without surfactant solution.

Table 6.3. Comparison between the means of oil recovery rates (ORR %) with surfactant and no surfactant for all sludges.

Sample	ORR% (water)	ORR% (with surfactant)[1]	p-values[2] (H_1: $\mu_d > 0$)
WSS	22 (± 1)	TX114 (2CMC) = 53% (± 2)	< 0.01
ODS	6 (± 0.15)	RL (0.5CMC) = 5% (± 0.87)	0.847
STS	60 (± 8)	RL (5CMC) = 76% (± 18)	0.132
RS	49 (± 2)	SDS (5CMC) = 52% (± 9)	0.749
NSC	59 (± 7)	RL (2CMC) = 51% (± 6)	0.795

[1] The highest ORR values were obtained from the surfactant concentration experiment (Figure 6.2). The S/OS ratios were obtained from the S/OS ratio effect experiment (Figure 6.1): ODS at 1:1; STS, RS, and NSC at 5:1 S/OS. Cyclohexane was added at 1:1 C/OS ratio. The standard deviation is shown (n = 3).
[2] The alternative hypothesis (H_1) tested if the difference (μ_d) between both means was higher than 0.

6.3.3. EPH concentrations of the recovered oil from different sludges

Figure 6.4 shows the EPH concentrations of the recovered oil in the surfactant concentration experiment. Only one replicate (n = 60) was analysed due to the high amount of samples if these were analysed in triplicate (180). The purpose of this analysis was to observe how the GC fractions are distributed in the recovered oil using different formulations of surfactants at various concentrations.

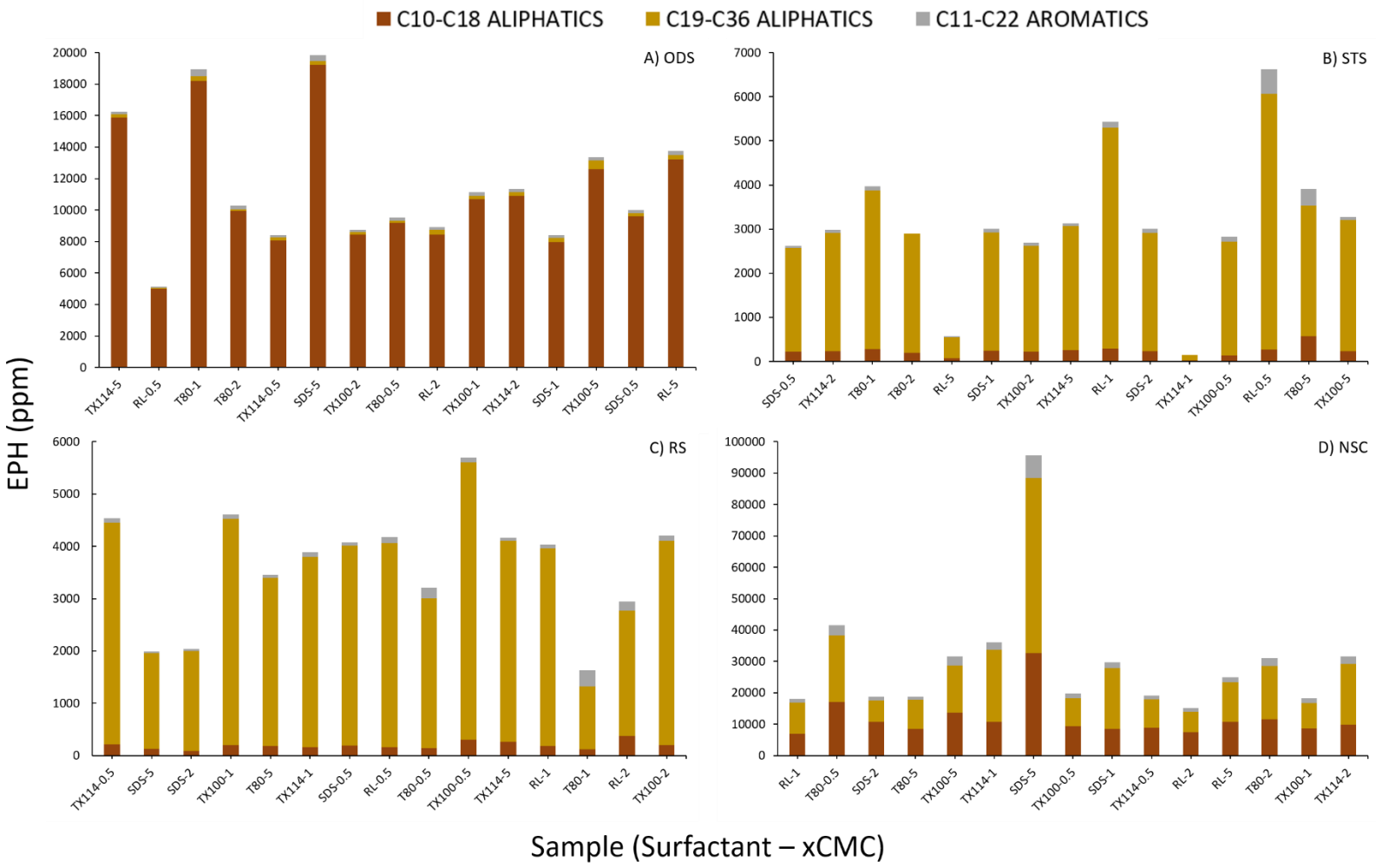

Figure 6.4. EPH concentrations of the oil recovered (surfactant concentration experiment) from the ODS (A), STS (B), RS (C), and NSC (D). Only one replicate per sample was analysed due to the high number of samples.

A one-way ANOVA revealed a highly significant effect of the type of sludge ($p < 0.01$) as a factor on the total EPH concentrations. However, the surfactant type and concentration factors were not significant different ($p = 0.946$ and $p = 0.808$, respectively). Consequently, the two-way ANOVA revealed no significance in all interactions: sludge * surfactant ($p = 0.682$), sludge * surfactant concentration ($p = 0.858$), surfactant * surfactant concentration ($p = 0.772$).

The relevance of this data is to assess if the recovered a crude oil had a potential of being reused as a feedstock for fuel production. For instance, an oil with higher concentration in the heavy oil fraction (e.g. C_{16}-C_{34}) can be used in the refinery and production of heavy fuel oil (Wang *et al.*, 2003). Likewise, if the recovered oil had a higher proportion of the light hydrocarbon fraction (C_{10}-C_{18}), this oil can be used as a feedstock to produce distillable products such as diesel (Giles, 2010). The highest total EPH concentration was from the recovered oil from NSC with SDS at 5CMC (total EPH concentration = 96,000 ppm). The other surfactants had total EPH concentrations less than 42,000 ppm.

For ODS, the highest amounts of recovered oil with TX114 (5CMC), T80 (1CMC), and SDS (5CMC) EPH concentrations were 16,000, 19,000, and 20,000 ppm, respectively. The lowest total EPH concentration was obtained with RL at 0.5CMC (5,000 ppm). When RL was used for washing the STS sludge, the highest total EPH concentrations were obtained at 0.5CMC (6,600 ppm) and 1CMC (5,400 ppm). However, when RL was added at 5CMC, the concentration was low (570 ppm). Also, the EPH concentration was lower with TX114 at 1CMC (140 ppm). For RS, the concentrations were lower compared to STS, in which the highest concentration obtained was 5,700 ppm when TX100 (0.5CMC) was added. Also, high concentrations were obtained using TX114 (0.5CMC) and TX100 (1CMC) in the OSW of RS with 4,500 and 4,600 ppm, respectively.

6.3.4. EPH concentrations in the OSW residuals-treated soils used for the toxicity tests

A previous analysis of some OSW-residuals obtained in Chapter 5 showed that the total EPH values were in the range of 2,500 to 3,000 ppm when TX100 at 2CMC and cyclohexane (2:1 S/OS ratio) were used. The total EPH concentrations in soils at different concentrations of OSW residuals are shown in Table 6.4. The total value of soil (0% OSW) was 13 (± 0.88) ppm and for the blank reference (sand) was 12 ppm. The sensitivity of the GC-FID was 0.5 ppm. A paired t-test ($\alpha = 0.05$) showed that the mean of the total EPH concentrations from most of the OSW residual-treated soils was not different compared to the mean of the non-treated soil control. Only, the means for STS-SDS at 5% and 10%-, STS-TX100 10% and 50%-, and RS-TX100 (5%)-treated soil were significantly higher than the non-treated control (Table 6.4). However, these values did not represent any relevant TPH contamination due to the reduced concentrations.

Table 6.4. Total EPH concentrations in soils after addition (%) of OSW residuals used in the toxicity tests.

Sample	Total EPH concentration (ppm) [1]
STS-RL (10%) [2]	14 (± 3)
STS-TX100 (5%)	13 (± 8)
STS-SDS (5%)	19 (± 2)
RS-TX100 (5%)	18 (± 2)
ODS-TX100 (5%)	20 (± 4)
STS-TX100 (10%)	18 (± 4)
STS-SDS (10%)	21 (± 2)
STS-TX100 (25%)	14 (±0.93)
STS-TX100 (50%)	17 (±0.64)

[1] The p-values from the paired t-test were obtained by comparing each of the mean values for the total EPH concentration from the residual-treated soils with the mean of the control without residual (13 ± 0.88 ppm). The alternative hypothesis tested if the difference (μ_d) between both means was higher than 0.
[2] Percentage of the addition of OSW residuals in soil.

6.3.5. Dehydrogenase activity (DHA) test of the OSW residuals in soil

Before the analysis of the toxicity of the OSW residuals added to soil, the effects of the incubation time on the DHA assay when conducted for soil and oil sludges (Figure 6.5) and OSW residuals (Figure 6.6) were tested.

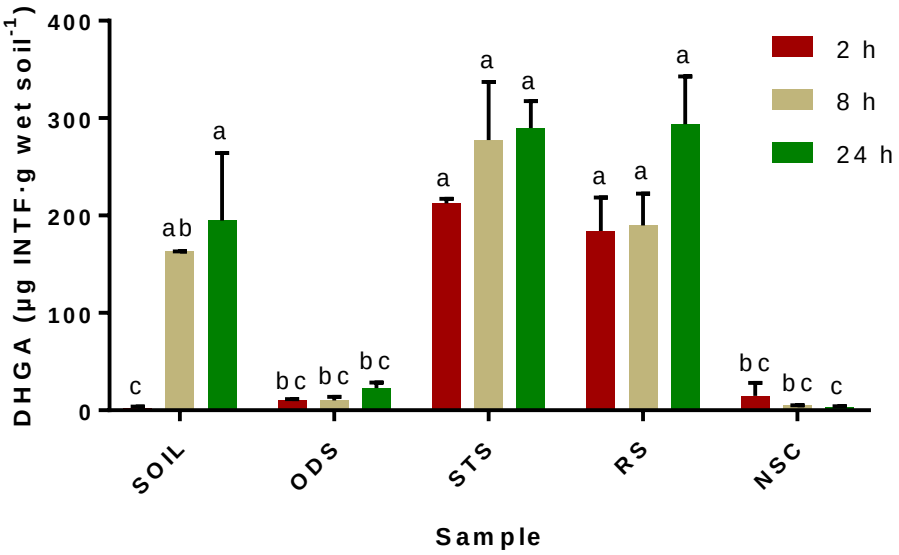

Figure 6.5. Dehydrogenase activity (DHA) of soil and oil sludges at different incubation times. The INTF concentrations were corrected with both biotic (without INT) and abiotic (with 0 h incubation time) controls. DHA mean values with the same letter are not significantly different; the comparisons of the samples (soil and oil sludges) with incubation times were analysed ($p > 0.05$; Tukey's test). The standard error of the mean (SEM) bars are shown ($n = 3$).

Figure 6.5 illustrates the effect of incubation time on the production of INTF as a result of DHA for the sludges (ODS, STS, RS, and NSC) and soil. A one-way ANOVA showed a highly significant effect on the sludges and soil ($p < 0.01$), and also for the time factor ($p = 0.001$). The interaction between the incubation times and the types of oil sludges was highly significant ($p < 0.01$). DHA for soil, ODS, STS, and RS increased with incubation time and had a detectable DHA at 24 hours. The DHA had a significant increase in the soil throughout

the different incubation times ($p = 0.002$) as expected due to increasing microbial activity in time. STS and RS had significantly higher DHA at 2 hours compared to soil, ODS, and NSC ($p < 0.01$). On the contrary, there was no significant decrease in the DHA with time in the NSC sludge ($p = 0.449$). However, the mean of DHA values at 8 h ($p = 0.004$) and 24 h ($p = 0.026$) were significantly higher than the 0 hours DHA value, except for the DHA value at 2 h ($p = 0.186$). Therefore, it can be inferred that NSC had detectable DHA values at 24 h.

The DHA for all the possible combinations of OSW residuals among all sludges and surfactants is shown in Figure 6.6. After correcting with the absorbance of biotic (without INT) and abiotic (with 0 h incubation time) controls, negative values in the INTF concentrations for some of the residual combinations were obtained. These values suggested that other chemical interactions unrelated to this test could have affected the measurement of the DHA. The negative values were due to the absorbances from the abiotic controls (zero incubation time) being higher than the absorbances at the different incubation times. ODS and STS residuals had a higher absorbance at 0 hours (Figure 6.7B and D) compared to the absorbance of soil at 0 hours (Figure 6.7A). However, there was a green colour in the ODS samples (Figure 6.7C). The green colour is starting to be detected at 490 nm (Clayden *et al.*, 2012). Since the absorbance was measured at 464 nm, this could indicate that there was some red colour overlapped with the green transmitted from the sample, then the red colour was detected at this wavelength. This green colour in the ODS residuals could be due to the tetrazolium salt from the INT that extracted copper salts from the sludge as reported by Altman (1976) and Obbard (2001). They mentioned the possible formation of chelates between copper ions (Cu^{2+}) and the formazans from the INTF.

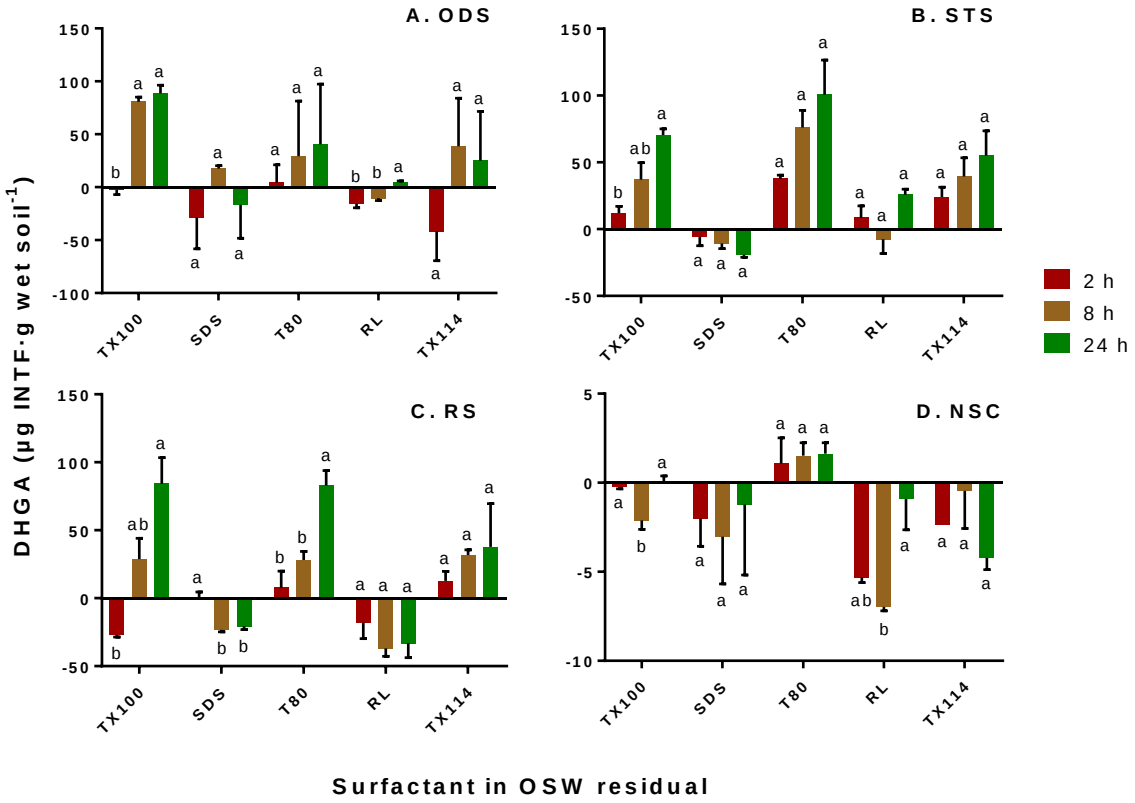

Figure 6.6. Dehydrogenase activity (DHA) in all type of OSW residuals from ODS (A), STS (B), RS (C), and NSC (D) at different incubation times. The INTF concentrations were corrected with biotic (without INT) and abiotic (with 0 h incubation time) controls. DHA mean values with the same letter are not significantly different; the comparisons of surfactants with incubation times per oil sludge were analysed ($p > 0.05$, Tukey's test). The standard error of the mean (SEM) bars are shown ($n = 3$). The negative values obtained did not mean a negative DHA; these values were due to a negative corrected absorbance after subtracting absorbance of the sample from the high absorbance in the abiotic control. The high absorbances in the control were caused by an unrelated chemical interference in the DHA test as mentioned in the text.

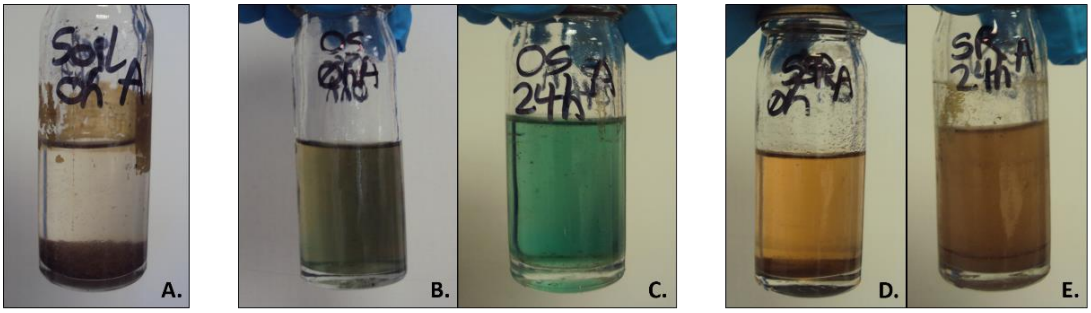

Figure 6.7. Colours observed in the OSW residuals after the addition of INT to soil at 0 hours (A), ODS-SDS at 0 hours (B) and 24 hours (C), and STS-RL at 0 hours (D) and 24 hours (E).

Similar to the determination of incubation times for all sludges, the interaction on the type of OSW residuals and the incubation time factor was significant ($p = 0.028$). In general, the OSW residuals with TX100, TX114 and T80 had an increase in the DHA through the time of incubation. However, the DHA of OSW residuals with SDS was not detectable as negative values were obtained impliying that other compounds (possibly from this surfactant) could be affecting the absorbance detection (Figure 6.6). A similar situation was observed with OSW residuals with RL since it was expected a higher DHA due to the low toxicity of this biosurfactant.

Also, negative DHA values were observed among the residuals from the washing of NSC, and they had the lowest DHA values compared to the other type of residuals (Figure 6.6D). The highest DHA values in the NSC residuals were obtained with T80; 1 (± 2) µg INTF·g wet soil^{-1} at 2 hours, and 2 (± 1) µg INTF·g wet soil^{-1} at 24 hours. However, these values were not significantly different from zero ($p = 0.266$ and $p = 0.058$, respectively), which suggests no detectable activity for all the residuals from NSC. Moreover, there was no differences among the incubation times ($p = 0.425$) for all the NSC residuals (Figure 6.6). Despite that it was proposed 48 hours of incubation time (Shaw and Burns, 2006), these results confirmed that there was a detectable INTF concentration at 24 hours. Therefore, this incubation time was selected for the next DHA tests of OSW residuals in soil to save some time during the experiments.

If the effects of all the OSW residuals in soil were analysed, the experimental effort in terms of material and sample amount would be high. The INTF of either STS or RS (sludges and residuals) was easily detected. In addition, these samples had less interaction with the DHA

test as it were found less negative values in the corrected absorbance values. Therefore, STS was selected as the sludge to obtain the residuals for the DHA assay in soil. TX100 was chosen as the surfactants because the DHA assays in the residuals were also easily detected (Figure 6.5 and Figure 6.6). Also, the effect of a toxic surfactant such as SDS was assessed for comparison. RL values at 10%, 25%, and 50% OSW residuals in soil were analysed to compare with a surfactant that is more benign to the environment. The effect of the increasing concentrations in the TX100-, SDS-, and RL-treated STS residuals on soil DHA is shown in Figure 6.8.

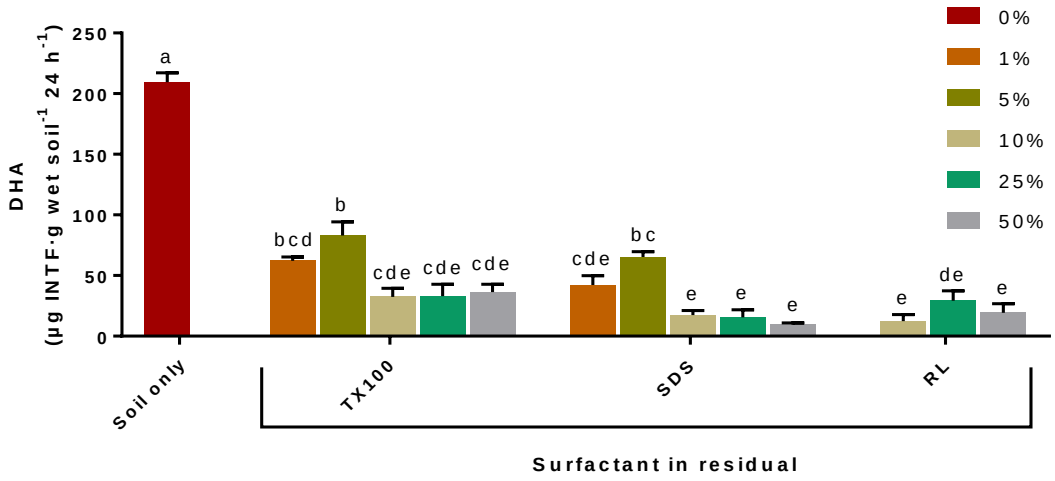

Figure 6.8. Dehydrogenase activity (DHA) of OSW residuals (with TX100, SDS, and RL at 5CMC) from the STS sludge at different percentages of addition into soil. The incubation time was 24 hours. The INTF concentrations were corrected with both biotic (without INT) and abiotic (with 0 h incubation time) controls. DHA mean values with the same letter are not significantly different; the comparisons of surfactants with the percentage of OSW residuals were analysed ($p > 0.05$, Tukey's test). The standard error of the mean (SEM) bars are shown ($n = 3$).

As opposed with the DHA analyses of sludges and OSW residuals, no interference was evidenced in the DHA tests of the soils with the residuals as both abiotic and biotic controls did not detect any chemical interactions unrelated to this test. The impact of the OSW residuals in soil was noticeable since the DHA for the soil sample (0% OSW residual) was 200 (± 10) µg INTF·g wet soil^{-1}. In general, the INTF production had a highly significant increase in the 1% and 5% of OSW residuals ($p < 0.01$) compared to the high concentrations (10, 25 and 50%).

A two-way ANOVA revealed a significant overall effect of the OSW concentration ($p < 0.01$) and type of surfactant ($p < 0.01$) as factors on DHA. However, the OSW concentration and surfactant type interaction term in the analysis was not significant ($p = 0.929$). A *post-hoc* analysis revealed that the DHA in the 5% OSW residual (the highest DHA among all OSW residuals) was highly significant different to the DHA in only soil ($p < 0.05$). Also, there were no differences in the DHA values among TX100-, SDS-, and RL-treated OSW residuals in soil at 10, 25, and 50%. The DHA values for 10, 25, and 50% RL-OSW residuals in soil were significantly lower than the TX100-OSW residuals at the same concentrations.

The DHA of some OSW residuals from all sludges added at 0, 1 and 5 % into the soil is shown in Figure 6.9. The effect of OSW residual type ($p = 0.001$) and soil concentration (%) ($p = 0.001$) was highly significant. A *post hoc* study of each residual (sludge-surfactant) confirmed that the DHA value at 0% OSW (only soil) was highly significant different compared to all the DHA values from OSW residuals ($p < 0.01$).

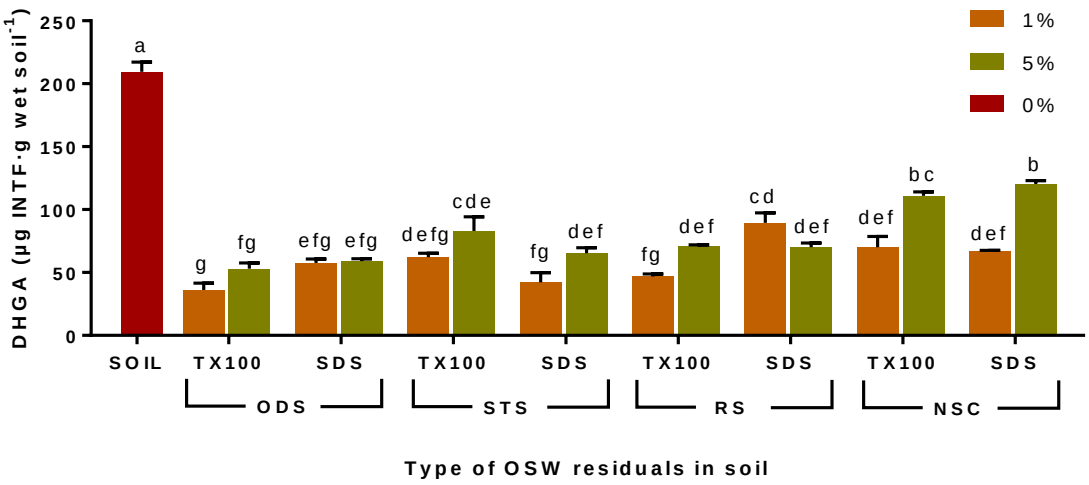

Figure 6.9. Dehydrogenase activity (DHA) of OSW residuals (with TX100 or SDS) from all sludges at different percentages of addition into the soil (% OSW). The incubation time was 24 hours. The INTF concentrations were corrected with both biotic (without INT) and abiotic (with 0 h incubation time) controls. DHA mean values with the same letter are not significantly different; the comparison of each residual (sludge + surfactant) with the percentage of OSW residuals were analysed ($p > 0.05$, Tukey's test). The standard error of the mean (SEM) bars are shown ($n = 3$).

The highest DHA from all of the OSW residuals was 120 (± 5) µg INTF·g wet soil^{-1} (NSC-SDS; 5% OSW). There were no significant differences between the TX100- and SDS-treated OSW residuals from the NSC sludge when these were added at 1% ($p = 0.75$) and 5% ($p = 0.09$). Only there was a highly significant difference ($p = 0.002$) between DHA values from RS with TX100 and SDS at 1%. The lowest DHA values were obtained from ODS-TX100 at 1% and 5% (36 ± 10 and 53 ± 8 µg INTF·g wet soil^{-1}, respectively). These values were significantly different (both with $p = 0.004$) to the above mentioned highest DHA value for NSC-SDS (5% OSW). Also, DHA values from STS-SDS (42 ± 13 µg INTF·g wet soil^{-1}) and RS-TX100 (47 ± 3 µg INTF·g wet soil^{-1}), both at 1% OSW in soil, were significantly lower ($p = 0.010$ and $p = 0.001$, respectively) compared to NSC-SDS.

6.3.6. Toxicity of OSW residuals in the germination of ryegrass

The range of temperature and relative humidity of the greenhouse throughout all the study was from 15 to 25°C and from 30 to 60%, respectively. The ryegrass seed germination stage finished on day seven as reported previously (Alvarenga *et al.*, 2016). The germination rate was higher than 70% at all the concentrations studied (Figure 6.10).

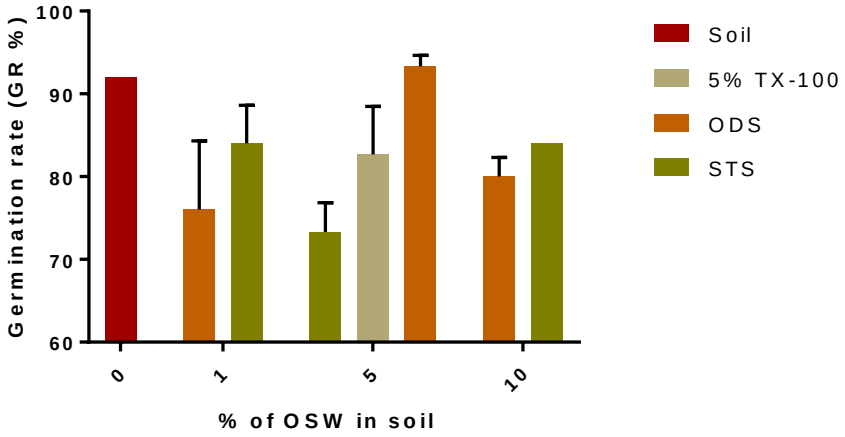

Figure 6.10. Germination rate at day 7 for different percentages (0, 1, 5, and 10 %) of TX100 (5CMC) ODS- and STS-treated OSW residuals in soil. A control of only 5% TX100 in soil is shown. The standard error of the mean (SEM) bars are shown (*n* = 3). The standard errors for 0% and 10% STS-TX100 in soil were zero because all replicates had equal germination rate values.

There was 92% of germination rate in only soil. The mean germination rate for the positive control (reference soil) was 83% (± 9). No germination (0%) was observed for the reference toxicant (diesel) and boric acid negative controls. There were no significant differences between the treatments with ODS and STS in all concentrations ($p = 0.764$). Also, the germination rate between the control with only 5% TX100 (83% ± 10) and 5% OSW residuals from both sludges were not significantly different ($p = 0.157$ and $p = 0.073$, respectively). Additionally, a paired t-test confirmed that there were no differences between each OSW residual and the TX100-treated soil ($p > 0.05$).

Table 6.5 shows the p-values of the paired t-tests performed between each concentration of OSW in soil and the mean of the germination rate with no OSW (92%). The germination rate was not significantly different at 1% OSW from both sludges, ODS and STS, amended in soil (Table 6.5). However, a potential negative effect of the residuals was detected in the germination rate at 5% of STS-TX100 ($p = 0.017$) and at 10% OSW for both ODS- ($p = 0.018$) and STS-TX100 ($p = 0.001$) residuals in soil.

Table 6.5. Germination rates for all the OSW residuals at 1, 5 and 10% in soil.

Residuals	OSW %	Germination rate[1]	p-values[2] (H_1: $\mu_d < 0$)
ODS-TX100	1	76 (± 14)	0.097
ODS-TX100	5	93 (± 2)	0.789
ODS-TX100	10	80 (± 4)	0.018
STS-TX100	1	84 (± 8)	0.113
STS-TX100	5	73 (± 6)	0.017
STS-TX100	10	84 (± 0.01)	0.001

[1] The standard deviation is shown (n = 3).
[2] The p-values from the paired t-test were obtained by comparing each of the mean values for the germination rate OSW residual-treated soil with the mean of the control without residual (92%). The alternative hypothesis (H_1) considered the mean difference (μ_d) between paired OSW treatments on each sludge.

The soil pH values before and after the germination test are shown in Table 6.6. In general, all values were close to the pH neutrality. Therefore there was no toxic effect from pH (ASTM-E1963-09, 2014).

Table 6.6. Soil pH values (before and after) for all treatments of the seed germination test.

Treatment	pH	
	Before	After
0% OSW	7.24	7.52
ODS-TX100 1%	7.64	7.88
ODS-TX100 5%	7.59	7.85
ODS-TX100 10%	9.60	8.40
STS-TX100 1%	7.04	6.86
STS-TX100 5%	6.81	6.59
STS-TX100 10%	6.78	7.04
TX100 5%	7.26	7.54
Control	7.09	7.22
Boron	7.49	7.60

The standard methods of the seed germination tests normally suggest the use of both monocotyledonous and dicotyledonous species. Therefore, this study included originally, *Lactuca sativa* as the representative of the dicotyledonous group. However, no germination was obtained in all treatments, even in the controls, due to issues with the seeds obtained commercially. In addition, since this test was the last experiment done in the thesis, the time was limited to repeat it with seeds from another source.

6.4. Discussion

6.4.1. Effect of S/OS ratio and surfactant concentration in the oil recovery from different sludges

The S/OS ratio factor was highly significant ($p < 0.01$). The various results obtained in these experiments, including the strong effect of the S/OS ratio factor and the type of surfactant in the oil recovery among the oil sludges, imply that there is a need to perform a bench-scale test of a sub-sample for each new oil sludge sample before treating all the sludge. Both, Deshpande et al. (1999) and Urum and Pekdemir (2004) concluded from their studies that since the surfactants had differential effects on different contaminated soil matrices, they recommended that it is necessary to do a bench-scale experiment to select the suitable surfactant for the washing.

An important result found in this thesis was that there were no differences in the ORR whether or not the surfactant solutions were added for the OSW. Only one (WSS sludge) of the five sludges analysed had a highly significant improvement in the oil recovery by using surfactants. Most of the studies reported an improvement in the removal efficiency of petroleum hydrocarbons by adding surfactants in the soil washing processes (Deshpande *et al.*, 1999; Urum *et al.*, 2004; Urum *et al.*, 2006; Peng *et al.*, 2011; Wu *et al.*, 2012). On the contrary, only a few studies reported a similar removal efficiency from soil washing between the surfactant and no surfactant treatments. Bhandari et al. (2000) reported no significant enhancement in the TPH removal from sand contaminated soils with a non-ionic surfactant blend (diethylene glycol butyl ether and ethoxylated nonylphenol) solution compared to the distilled water control at neutral pH. Only the removal with surfactants improved when the pH was raised to 12 (Bhandari *et al.*, 2000). Also, in another study, there was no difference on the crude oil removal from the soil when only water was used compared to other biosurfactants (aescin, lecithin, saponin and tannin) and SDS (Urum and Pekdemir, 2004). Likewise, a washing study from a diesel-contaminated soil found a lower TPH removal with non-ionic surfactants compared with the control with distilled water (Hernández-Espriú *et al.*, 2013). The non-ionic surfactants included Tween 80 and 20, a zwitterionic surfactant (Polafix CAPB), and a poly (ethylene oxide) surfactant. The TPH removal with these surfactants was less than 20% compared with a 40% removal using distilled water only.

The oil recovered from RS and STS had some water in the oil layer implying a stronger O/W emulsion in the sludge. Hu et al. (2015) experienced a similar situation where some remaining water was recovered in the top oil layer. They also measured the recovered oil by weight similar to the method performed in this thesis. Indeed, the authors mention that having water in the recovered oil could lead to an overestimation of the oil recovery rate. However, they claimed that this will affect the overall oil recovery results minimally because all samples were treated equally by homogeneous mixing of the oil sludge, and always the same quantity of oil sludge was used (Hu *et al.*, 2015). Indeed, this was not the exception throughout this whole thesis, as all of the samples were prepared following the same protocol, and also, the same proportion of oil sludge was kept in all experiments (i.e. one part of sludge combined with a different number of volumes of surfactant solution). Besides, the amount of water in the oil was negligible compared with the quantity of recovered oil.

When RL was used in the washing of both sludges, it was found that the biosurfactant breaks the emulsion in RS and STS as the recovered oil was more viscous and with no visual evidence of water. Long et al. (2013) reported the role of rhamnolipids in the demulsification of waste crude oil, and more than 90% of water was removed. Sha et al. (2012) linked the high surface activity of RL with its ability of breaking the interfacial film in the emulsion.

6.4.2. Variation of EPH concentrations among the recovered oil samples

Although there were no significant differences in the ORR values between using surfactants and water in the washing of the sludges, the EPH concentration data from all samples is relevant under the light of the potential reuse of the recovered oil. The inter-surfactant and inter-sludge variations in the EPH concentrations from the recovered oil indicates the importance to pre-test different surfactant formulations. In this study, TX114 (5CMC), T80 (1CMC), and SDS (5CMC) in ODS, RL (0.5 and 1CMC) in STS, TX100 (0.5CMC) in RS, and SDS (5CMC) in NSC were the potential surfactant formulas that can be used to recover higher EPH concentrations in the recovered oil from each type of the sludges. A specific formulation of surfactant can be used to obtain higher concentrations of light aliphatic fractions that are more suitable for fuel production. Also, it is important to determine the concentrations of each hydrocarbon fraction for toxicity reasons. For example, by assessing

the aromatic fraction, PAHs can be analysed, as these compounds are catalogued as genotoxic to humans, especially the high-molecular weight PAHs (Robertson *et al.*, 2007).

According to Hu et al. (2015), the oil quality can be evaluated with the EPH content from the GC profiles. However, this assumption has to be carefully considered because Giles (2010) claimed that gas chromatography data is not a direct measurement of oil quality, as the sample has to be fractionated by distillation methods to confirm quality. Additionally, other physicochemical properties such as the API gravity, pour and flash point, heat of combustion and sulphur content have to be done for a direct and complete analysis of the quality of the oil (Abouelnasr and Zubaidy, 2008; Zubaidy and Abouelnasr, 2010; Hu *et al.*, 2015). Villalanti et al. (2006) mentioned that gas chromatography is a rapid method to determine the compounds in oil and that this data can help to select the most economic favourable crude oils in terms of a potential refining. To avoid further confusion, the use in this thesis of the GC profile per se will not be considered to be an absolute confirmation of the quality oil. Rather these data will be used to see potential reuse of the oil in the refining and production of fuel.

6.4.3. Total EPH concentrations in the OSW residuals and the residual-treated soils for the toxicity tests

The total EPH concentrations from the OSW residuals varied from 2,500-3,000 ppm. Moreover, the concentrations in the OSW residuals-treated soils were lower than 20 ppm. These values did not represent any relevant TPH contamination due to the reduced concentrations. No significant differences were found compared to the non-treated soil, except for the soils treated with STS-SDS at 5% and 10%, STS-TX100 10% and 50%, and RS-TX100 (5%), which were highly significant. These values were lower than the recommended clean-up level of 10,000 ppm in soils close to industrial areas (Shelley *et al.*, 1997), suggesting that no further treatment is required to decrease the TPH concentrations in the residuals.

Since this thesis was focused on the organic chemical contamination in the sludges, there was no after OSW-metal concentration data of the recovered oil and OSW residuals. Only the heavy metal concentrations were analysed in the original sludges before the oil sludge washing process, but the concentrations were below the established limits except for nickel (See Chapter 2, Section 3.3.2.2).

6.4.4. Toxicity tests of the sludges and OSW residuals

Experiments were conducted to determine whether the oil sludge washing process resulted in the production of a residual with toxicity which is reduced compared to the initial sludge and whether OSW residual toxicity depends on the surfactant used. Soil-based assays (DHA and germination of ryegrass) were used as the toxicity assessments following the scenario of the disposal and further treatment of the OSW residuals via landfarming. Before the impact of the OSW residual amendment of soil was investigated, preliminary experiments were conducted to test if there was any DHA associated with the sludges and residuals themselves.

The DHA test measures the soil aerobic microbial respiration by assessing the activity of the dehydrogenase. Therefore, two elements are crucial for this test to get a genuine recordable activity, by having microorganisms in numbers sufficient to produce detectable respiration and also an electron donor for respiration to occur (organic carbon but also potentially inorganic sources – NH_3, sulfur). This test uses the INT as an artificial electron acceptor. The DHA activity can be confounded with a biotic reduction from non-related soil microorganisms, so it is important to work with sterilised materials. Also, the abiotic reduction can affect the test by the production of compounds that absorb at 464 nm that are unrelated to INTF formation. Therefore, this study used both abiotic and biotic controls as explained in section 6.2.3.2.

Initial analysis of the DHA associated with the sludges before the washing process revealed that the there was almost no detectable DHA in the ODS and NSC sludges. However, the apparent DHA for STS and RS was higher than the activity in the non-amended soil, even at time 0, indicating spurious activity due to the occurrence of chemical reactions unrelated to DHA and not detected by the abiotic controls. Any detectable DHA in sludges and OSW residuals indicated the potential use of hydrocarbons as a carbon source by the microbial hydrocarbon degraders (Serrano *et al.*, 2008). Therefore, the highest DHA concentration in NSC-SDS and –TX100 (Figure 6.9) was possible due to the presence of microorganisms resistant to oil contamination (i.e. use of crude oil as carbon source). In some OSW residuals, such as ODS-SDS (Figure 6.6A) and RS-SDS (Figure 6.6C), it was found lower DHA values at 24 hours of incubation. This finding implies that some process has consumed the INTF produced at earlier incubation times. Here this thesis presented cases where the DHA test can

overestimate (STS and RS sludges) and underestimate (OSW residuals; ODS-SDS) the microbial activity. Although this is a drawback of the test of the oil sludges and OSW residuals, this interference was not a problem when OSW residuals mixed with soils were analysed as both abiotic and biotic controls did not detect any chemical interactions unrelated to this test.

As mentioned before, usually there is co-contamination of inorganic and organic compounds in the oil sludges. In this thesis, the oil sludges had the presence of metals as reported in Chapter 3 (Section 3.3.2.2). Although no metal analysis was done in the residuals, it was detected some interference of copper (Cu) with the INT in the residuals from ODS-SDS (Figure 6.7B and C). For reference, the copper concentrations in the original sludges used in the DHA tests were for 8 ± 0.08 $\mu g \cdot g^{-1}$ for ODS, 7 ± 0.20 $\mu g \cdot g^{-1}$ for STS, and 12 ± 0.80 $\mu g \cdot g^{-1}$ for RS. It was reported before that there was an interference of copper ions in the DHA test of sewage sludges-treated soils contaminated with heavy metals (Chander and Brookes, 1991; Chander *et al.*, 1995). These authors used a similar type of tetrazolium compound, the 2,3,5-triphenyltetrazolium chloride (TTC), that converts to triphenylformazan (TPF), but they did not find an effect of Zn, Ni and Cd in the DHA test. Chander and Brookes (1991) were the first to show the underestimation of the DHA test with TTC due to copper ions. Moreover, Obbard (2001) confirmed this interference using INT, and the author also did not find any effect of Zn, Ni and Cd in the DHA, except for Cu.

The impact of the residuals in the soil was evident since the DHA for only soil was highly significantly different compared with the other concentrations of residuals (%). This reduction of DHA implied some degree of toxicity of the residuals to the microorganisms. However, some DHA was detected, so additional bioremediation processes can be applied to treat these residuals further. Particularly, it was found that the DHA values for RL at 10, 25, and 50% OSW residuals in soil were significantly lower than the TX100 OSW residuals at the same concentrations. Marecik et al. (2012) found that increasing concentrations of RL can be toxic by affecting the germination index and growth of plants such as alfalfa, sorghum and mustard, and also by altering the microbial activity. One reason that could explained this toxicity of RL is that this biosurfactant can change the permeability of the cell membranes allowing the interaction of the contaminant with the cells (Marecik *et al.*, 2012). Also, the positive interaction between RL and the oil droplets can make the contaminant more bioavailable (Mueller *et al.*, 1989; Chrzanowski *et al.*, 2009).

In general, no significant differences in the DHA among concentrations were found among the different concentrations tested. For example, this event was observed in the 10%, 25% and 50% OSW residuals from STS in soil (Figure 6.8). Similarly, it has been reported in other studies that the amount of contaminant load in a matrix is occasionally not linked to its toxicity (Domene *et al.*, 2008a; Domene *et al.*, 2008b; Roig *et al.*, 2012; Alvarenga *et al.*, 2016). One factor that could contribute to this event is the degree of chemical stabilisation of the contaminant in the sludge as mentioned by Roig et al. (2012) and Alvarenga et al. (2016). For example, chemical stabilisation can be achieved by allowing more interaction time between the contaminant and soil, and also by adding chemicals such as pH neutralisers or organic compounds to reduce toxic effects of some chemicals present in the sludges. However, since these sludges were mixed with soil and left overnight, it is difficult to explain if the stabilisation or maturation of the chemicals or contaminants present in the sludge can contribute to a lower toxicity. Therefore it is recommended to test the effect of weathering or ageing of the residuals in soil in further studies (Tang *et al.*, 2012).

The germination rate of ryegrass was higher than 70% for all concentrations. These results are acceptable because the control showed no sign of phytotoxicity, and the germination rate was greater than the reported percentage germination standard of 75% in the controls for ryegrass (USEPA, 2006). Also, the toxicity data is valid since the pH for all the samples before and after the experiment was between 4 and 10, so a pH toxicity effect can be ignored (ASTM-E1963-09, 2014). Moreover, there was no germination in the negative controls as expected. There was a significant decrease in the germination rate of 5%- and 10%-OSW residuals in soil. However, this cannot be fully attributed to EPH contamination as this was lower than 20 ppm for the tested samples (Table 6.4). Therefore, other factors could be contributing to this decrease such as the co-contamination with chemical additives in the STS sludge and some PTEs (Chapter 3, Section 3.3.2.1). Furthermore, it is recommended to perform root length, shoot height, and dry total mass measurements of the seedlings (ASTM-E1963-09, 2014) to confirm that the plants are not sensible to the OSW residuals.

Indeed, the use of the lettuce could be ideal for this experiment to test the effect of these residuals from oil sludge due to the known sensitivity of this plant to petroleum contaminants (Banks and Schultz, 2005). On the other side, ryegrass has been reported to be tolerant to petroleum hydrocarbons (Olson *et al.*, 2003; Kaimi *et al.*, 2006; Barrutia *et al.*, 2011). Then, the data presented in this study can support the use of ryegrass in further treatments of the residuals (e.g. phytoremediation) if needed.

6.4.5. Further comments

The main aim of the OSW process is to recover the oil from the sludge for two reasons. First, this recovered oil can be reused as a feedstock for fuel production, such as diesel. Second, the contaminant levels of the residual sludge can be reduced. Sometimes, this residual sludge can still contain some contaminants that are strongly bound to the remnant sludge particles. Therefore, in this case, it is necessary to find further treatment methods for these OSW residuals. For instance, bioremediation techniques could be applied to treat these residuals while some economic benefits can be obtained at this stage. Therefore, it was proposed to implement a phytoremediation process using species of economic interest such as soybeans which are used for biodiesel production. As demonstrated in this chapter, the output from the chemical and ecotoxicity tests of the OSW residuals can elucidate any presence of contaminant and any detrimental effect to the organisms studied, respectively. Indeed, these results can decide if any further treatment of the residuals is needed.

Although this chapter had two different stages, the OSW for oil recovery purposes and the analysis of OSW residuals, some connections can be elucidated between both stages. First, it was found a justification to perform the OSW as the DHA was lower compared to the control with only soil (Figure 6.5) which implies the ecotoxicity of thee sludges. However, the STS and RS sludges gave a misleading higher DHA compared to the control due to some chemical interference. In fact, this chemical complexity of the sludge was observed in the OSW because the recovered oil phase had some water and sediments probably due to a strong O/W emulsion of these sludges. Conversely, when the DHA was analysed for the OSW residuals from the STS and RS sludges, it was found fewer interferences in the test compared to the other residuals from the other sludges (Figure 6.6). This situation implied that some of this so-called chemical interference was retained in the recovered oil phase due to the stronger O/W emulsion that affects the oil recovery. Also, the higher chemical interferences in the DHA test found in the residuals from ODS and NSC can be related to some event during the OSW that could expose these interferences in the residuals.

Since the ODS sample was obtained from an oil drilling process, the residuals had a higher amount of sediment and a less amount of recovered oil after the OSW process. This presence of sediment could increase the probability of chemical interference with the copper in the OSW residuals as shown in the pictures from Figure 6.7 and in the misleading negative

values found in the DHA test (Figure 6.6A). The fact that this effect was not found in the DHA test of the ODS sludge implied that these interfering chemicals became bioavailable during the OSW process as mentioned before.

Also, the data from the oil recovery tests showed that there was a highly significant effect of the type of sludge, but there were no significant effects of the surfactant type and concentration factors. Similarly, it was found this highly significant effect in the DHA tests, as there were significant differences among the sludges in this toxicity test for the sludges (Figure 6.5) and the OSW residuals (Figure 6.6), and also in the analysis of the OSW residuals-treated soils (Figure 6.9).

6.5. Conclusions

The main results obtained in this chapter are that the S/OS ratio had a high effect on the oil recovery, and the surfactant concentration had no effect on the oil recovery. The latter finding was confirmed by the fact that there was no significant difference in the ORR between the washing with and without surfactant solution. This result was found for four of the five oil sludges analysed in this thesis. Only, there was a highly significant ORR when surfactants were added in the OSW of the WSS sample.

Since this research was focused on the oil recovery and the organic contamination in the sludges, the metal component of the oil sludge was not studied in detail. However, the results showed that the initial metal concentrations of oil sludges were lower than the accepted levels of heavy metals in sludges that can be used as an amendment in agriculture (for more details see Chapter 3). Further studies can be aimed to assess the role of metals after an oil sludge washing process.

Indeed, the complexity of the oil sludges was evident since the copper present in the ODS sludge appeared to interfere with the dehydrogenase activity test. According to the results of this chapter, it is recommended to do only the DHA test in the soils treated with either the sludges or OSW residuals as the chemical interference was not strong. If the microbial activity has to be tested directly in sludges and residuals, other methods different to the DHA test should be used. For instance, other methods can test the activity of other enzymes such as invertase and catalase (Chander and Brookes, 1991). Also, other toxicity methods such as earthworm

mortality, inhibition of luminescence from *Vibrio fischeri,* and *Daphnia magna* immobilisation (Alvarenga *et al.*, 2007; Alvarenga *et al.*, 2016) can be undertaken to have a wider overview of the toxicity in other types of organisms.

In summary, since the S/OS ratio and type of surfactant were the factors with the strongest effects on ORR, it can be suggested some general recommendations to test the possibility of performing OSW in a new oil sludge sample. First, a quick bench scale experiment can be done to assess the ORR with and without surfactant at a low and high S/OS ratio (e.g. 1:1 and 5:1 S/OS). By doing this first assay, the need for the surfactant can be established. If it is not required, the costs can be reduced. For this first assay, the surfactant can be added at lower concentrations, as the results of this thesis showed no significant difference in the surfactant concentrations. If a surfactant is needed, the added value of this compound is the selective extraction of the oil fractions which may improve subsequent refining. Finally, it was demonstrated that the OSW residuals impacted the aerobic microbial oxidation activity significantly in soil. However, some DHA was detected in this study, and the results from the EPH data in the residual-treated soils were low. Therefore, a bioremediation process can be considered as a further treatment of these OSW residuals.

Chapter 7 - Conclusions and future directions on oil sludge washing

This final chapter synthesises the answers to the initial research questions by discussing the main results obtained in the thesis. This chapter also gives recommendations and future directions on the oil sludge washing process as a pretreatment of oil sludges. Furthermore, the possibility of applying this treatment at a large scale is discussed including the practical and economic feasibilities.

7.1. Research questions

The principal question of this thesis was whether the addition of surfactants and co-solvents in the oil sludge washing process enhances the recovery of oil and reduces the burden of hydrocarbon contamination. Five sub-questions were answered in this thesis.

The following are the answers to these five questions:

Q1) How do the surfactant type, surfactant concentration, and S/OS ratio factors affect oil recovery from different sludges in the OSW process?

- The interaction among the surfactant type and concentration and the S/OS ratio was significant. Particularly, it was found that the S/OS ratio had the strongest effect on maximising the oil recovery in the pilot study using a Taguchi experimental design. Moreover, this factor was significant in the final OSW experiment with four sludges. The oil recovery varied among the surfactants used in each sludge, but the surfactant concentration did not have an effect in the ORR. Moreover, there were no significant differences between using a surfactant solution and only water for all the sludges, except for WSS. This latter finding was surprising. Indeed, it was expected a significant improvement in the recovery by using surfactants in all the analysed sludges.

Q2) Do the physicochemical characteristics of surfactants and the mixture of two surfactants influence the efficiency of oil recovery in the OSW?

- Yes, it was found that physicochemical characteristics (micelle size, surface activity, viscosity, molecular weight) could be associated with the performance of the oil recovery. However, this assumption depends on the oil sludge being treated. For instance, it was found that the TX114 and RL, which had the biggest micelle size, had higher ORR values in most of the oil sludges. Also, TX100 had a high oil recovery, but his micelle size was smaller, implying that other factors such as HLB and molecular weight influenced in the oil recovery. For example, T80 had a bigger micelle size than TX100, but the oil recovery of the former was lower than the latter. In summary, RL, TX114 and TX100 had the highest surface activity, higher surface tension reduction in water, and the lowest CMC. Moreover, these surfactants had the highest oil recoveries as mentioned before. The addition of another surfactant did not significantly enhance the oil recovery from the oil sludge WSS sample. However, it has to be considered that this experiment was done for only one sludge (WSS) because the time and sample were limited to perform this experiment in the other four sludges. The oil recovery rates were not significantly different among the surfactant mixtures, and there was no enhancement in the oil recovery from the oil-water separator sludge (WSS sample) using the mixtures.

Q3) Are there any differences in the oil recovery of the co-solvents applied in the OSW with surfactants?

- Yes, the oil recovery values were different among the various co-solvents. Cyclohexane and toluene had the highest ORR, whereas pentane, hexane and iso-octane had the lowest recovery values. Since toluene was the first co-solvent used in this thesis (Chapter 4), the most important result was that cyclohexane (a solvent more benign to the environment) was not significantly different in the oil recovery compared to toluene. Therefore, cyclohexane was selected for the next OSW experiments with the other sludges.

Q4) Are the residuals from the OSW (residual sludge with surfactant solution and sediments from sludge) toxic to the soil microbiota and ryegrass?

- No, because it was detected some DHA in the soil microbiota, and the ryegrass had a germination rate higher than 70% with no evident signs of phytotoxicity. Although a negative impact on the soil microbiota was noticed with the DHA test, some DHA activity could still be detected. However, the reduction of DHA is an indicator of some degree of toxicity of the residuals.

Q5) What are the practical and economic feasibilities of OSW?

- The practical and economic feasibilities of OSW are discussed later in this chapter (Section 7.7).

Before discussing the findings in each question, it is necessary to recall the procedure done to respond to these questions. First, a pilot study (Chapter 4) was undertaken with the WSS sludge to test the effect of the three evaluated parameters in the OSW process (surfactant type and concentration, and S/OS ratio) using toluene as the co-solvent. At this point, Q1 (interaction among these parameters in the OSW) and the first part of Q2 (influence of physicochemical characteristics in oil recovery) began to be answered. Then, the best surfactants and their concentrations along with the best S/OS ratios were established for WSS. Second, the effects of the co-solvents (Q3) and the surfactant mixtures (second part of Q2) on OSW were tested in the same sludge (WSS) using the best conditions of the OSW parameters obtained from Chapter 4. At this point, it has to be mentioned that it was difficult to find more sludges. Later, more sludges were sourced (ODS, STS, RS, and NSC), so Q1 and the first part part Q2 (influence of physicochemical characteristics in oil recovery) could be more fully addressed. Consequently, it was acceptable to only focus on these questions, since it was proved with Q3 that cyclohexane, a more benign to environment co-solvent, could be used instead of toluene. Also, the second part of Q2 (surfactant mixtures) was not tested again in the other sludges because no significant effect of the surfactant mixtures was found for WSS. Probably this effect could be different in the other sludges, but the main objective of this study was to test the three parameters in the OSW. Also, this would have added an unnecessary extra complication for the experimental design because besides the three OSW parameters, the

sludge type would introduce an additional factor increasing the number of experimental runs. Also, the use of a surfactant mixture would raise the cost of the process. Despite that it was found a higher oil recovery rate at 2:1 C/OS, only the 1:1 C/OS ratio was used in the experiment with the other sludges (ODS, STS, RS, and NSC). Then, the data from these sludges could be comparable with the WSS data as its OSW parameters were only tested at 1:1 C/OS. Although the co-solvent used with WSS was toluene, it was demonstrated that the ORR value was no different from cyclohexane (co-solvent used with the other sludges). Therefore, these solvents were comparable to each other. Q4 was answered using the OSW residuals from the last oil sludge washing experiment with all sludges, except for WSS. Since this was the first oil sludge sample tested in Chapter 4 and 5, there was no more sample left for the toxicity tests. Finally, the practical and economic feasibilities of the oil sludge washing process at a large scale are discussed later in this Chapter (Section 7.7).

According to these answers, especially from Q1, although no difference was found in the oil recovery using surfactants, except for WSS (which had a highly significant oil recovery with surfactants), there were some variances in the recovery of oil fractions using different surfactants. This finding is crucial in terms of the possible reuse of the recovered oil.

Based on these results, the answer to the general question, “does the addition of surfactants and co-solvents in the oil sludge washing process enhance the recovery of oil and reduces the burden of hydrocarbon contamination”, is yes. Although only one sludge (WSS) had higher significant recoveries with surfactants and there was no difference of either adding or not any surfactant solution in the other sludges, it was found that the addition of surfactants could potentially improve the recovery of oil fractions favouring the potential reuse of oil. Also, there were differences in the ORR values among the co-solvents. Moreover, cyclohexane, a more benign to the environment co-solvent, had comparable results with toluene. In addition, all these findings suggested the uniqueness of each oil sludge. Therefore, it is recommended to test first if the application of surfactants improves the oil recovery from each oil sludge sample.

The following sections will discuss in detail the answers to the questions and the most relevant findings of this thesis.

7.2. RL, TX100 and TX114, enhancers of the oil recovery from oil sludges

Since the WSS sludge was the first sample collected, this sludge was used for the optimisation of the OSW parameters (surfactant type, S/OS, and surfactant concentration) in Chapter 4 and the co-solvent and surfactant mixture effect (Chapter 5). To our knowledge, no previous study has investigated only these parameters and their effect in a washing process of oil sludges from oil-water separators (WSS). The highest ORR values obtained at this stage are shown in Figure 7.1.

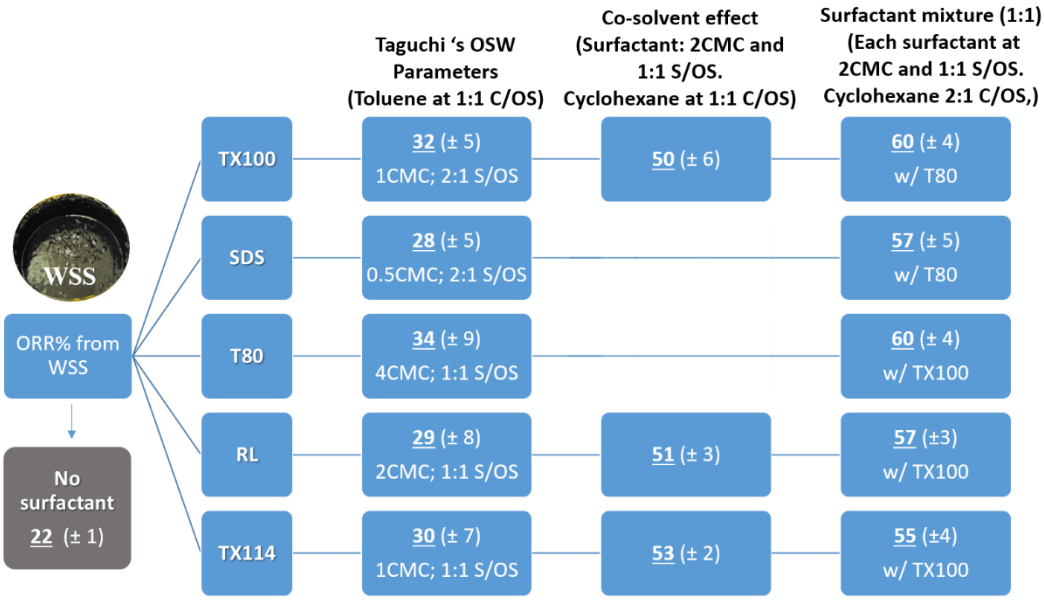

Figure 7.1. Flow chart with the highest mean ORR (%) values from WSS (oil-water separator sludge) obtained at each OSW experiment on Chapters 4 and 5. The mean values are underlined and in bold.

The oil recovery values obtained with WSS at the different stages were different. Also, these values were significantly higher compared to the value with no surfactant, as it was mentioned before. In addition, the C/OS ratio can be increased to 2:1 C/OS or higher to improve the oil recovery. For instance, when cyclohexane was added at 2:1 C/OS, the ORR were 56.77% (± 4.14) for TX100, 63.46% (± 1.89) for RL, and 63.43% (± 3.37) for TX114.

In the second stage of this thesis, other four sludges (ODS, STS, RS, and NSC) were used in the differential analysis of the OSW. Cyclohexane was used as the co-solvent added a 1:1 C/OS to have consistency with the data from WSS. The highest ORR values are shown in Figure 7.2. In general, RL, TX100 and TX114 were the surfactants with the highest ORR values in all sludges. The physicochemical characteristics of these surfactants predicted their best performance in the OSW. For instance, the three surfactants had the lowest CMC and micelle size (except for TX100, which micelle was smaller than T80); they had the highest surface activity and surface tension reduction in water. Particularly, SDS had the highest ORR value in RS. However, its micelle size and surface activity was the lowest among all surfactants. Also, the CMC of SDS and its surface reduction in water were the highest. An added value of RL, TX100 and TX114 is that these surfactants are more benign to the environment compared to SDS.

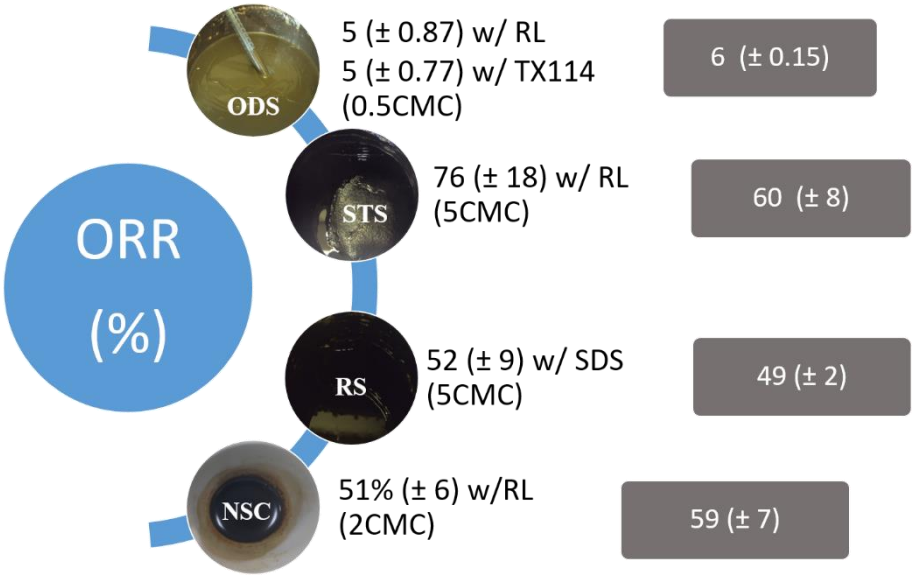

Figure 7.2. Radial diagram with the highest ORR (%) values from ODS, STS, RS, and NSC obtained at the OSW experiment on Chapter 6. The S/OS ratio used for STS, RS, NSC was 5:1, except for ODS (1:1 S/OS). ORR values in the grey boxes corresponded to the OSW control with water and no surfactant.

Despite that most of the ORR values with surfactants were higher than the values without surfactant, these values were not significantly different. This result was evident in general in all of these oil sludges, since the surfactant concentration factor did not affect the oil recovery.

7.3. Cyclohexane as an alternative co-solvent in the OSW

The OSW method applied on a bench scale in this thesis was performed in a closed system in which the vials had lids. Also, it is proposed later (Section 7.7) the use of a closed system for the application of this method at a large scale. By doing this, there is a low risk of any leakage of the materials used in the washing of oil sludges. Even though the OSW is applied in a closed system, toluene has potential higher harmful effects compared to cyclohexane if it is exposed accidentally to the environment. According to Henderson et al. (2011), cyclohexane is more benign to the environment and less harmful to human health compared to toluene. For instance, cyclohexane has lower impact scores on the environment and human health compared to the high impact scores for toluene (Table 5.1). Under these premises, it was proposed that cyclohexane can be used as an alternative co-solvent to toluene in the next OSW experiments for the other sludges, as the ORR values were not significantly different between these co-solvents. Another benefit of using cyclohexane was that the freeze/thaw step was removed from the OSW protocol (Section 4.2.3). In fact, cyclohexane has a higher freezing point (6.47 °C) compared to toluene or the other co-solvents used in this thesis (< -90 °C).

7.4. S/OS ratio as a crucial parameter in the OSW

The S/OS ratio was the parameter with the highest influence in the OSW. In addition, this factor was dependent on the type of oil sludge. This thesis has demonstrated, for the first time, that a higher S/OS ratio does not necessarily lead to increased oil recovery. This finding was evidenced with the WSS and ODS sludges because the highest recoveries were obtained at 1:1 S/OS ratios. The only case that the S/OS ratio did not affect the oil recovery was for NSC; there were no differences between low and high S/OS ratios. This fact confirmed that since every sludge is unique, it is necessary to test each sample before the application of OSW as a pretreatment of oil sludges.

7.5. The alternative experimental designs can reduce costs and time

The selection of the experimental designs used in this thesis was very advantageous in terms of costs and time. By doing this, the number of experimental runs was reduced, and the main effects could be detected. As previously reported by Yan et al. (2012) and Zheng et al. (2012), it was demonstrated that the Taguchi experimental design was a robust method to test the OSW parameters rapidly. The Taguchi design can be applied at early stages of experimentation, especially when there are several surfactants types and concentrations, and some oil sludge samples. The D-optimal design applied in the last stage of this thesis was well supported by using the data from the previous OSW experiments (Chapters 4 and 5) as an input for the design's model. The D-optimal experimental design was approximately 90% efficient. Certainly, these findings suggested that alternative experimental designs to the full factorial design can be used to evaluate the performance of different parameters in the OSW.

7.6. Further comments and recommendations

7.6.1. Oil sludges and the difficulty of finding samples

It was necessary to analyse oil sludges from different sources, so the performance of the OSW could be evaluated in various situations. Therefore, an effort was done to find various types of oil sludges. However, it was difficult to find samples as most of the contacted companies did not reply to the request. It was much easier to find oil sludges by contacting waste treatment companies because the names of the waste producers-oil companies were confidential. In addition, sometimes there was not enough sample available. For instance, the amount of the NSC sample was very limited, which was almost enough for all of the tests done including the OSW and toxicity tests, which were the priority assays. For this reason, it was not possible to analyse the trace metals content in the NSC sample due to the limited amount of this sample, as the OSW experiments and toxicity tests were more relevant to answer the research questions.

7.6.2. The use of toxicity tests as a complement of chemical tests to establish further treatments of the OSW residuals

Soil microbiota and ryegrass were used in this study as the test organisms for the toxicity assays of OSW residuals amended to soil. It was found that the residuals impacted the soil microbiota negatively. However, some DHA was detected suggesting the presence of some microbial activity. This finding implies that these OSW residuals could be further treated with bioremediation techniques. In addition, the high germination rates of the ryegrass in the OSW residual-amended soils obtained in the study suggest that a phytoremediation process could potentially be applied. Moreover, it is recommended to perform some root length, shoot height, and dry total mass measurements of the seedlings to confirm this information. Since the oil hydrocarbon burden of the residuals in soil was very low, other co-contaminants in the residuals such as inorganic contaminants could contribute to some of the observed toxicity. Moreover, although the plants used for the phytoremediation process cannot be used after as food supply due to possible accumulation of contaminant in the plants, some species with another economic benefit such as soybeans, can be used for biodiesel production (Liu *et al.*, 2010).

The DHA test was effective when evaluating the OSW residuals in soil. However, there was a high interference with the test when the sludges and its OSW residuals were assessed directly. For instance, the presence of copper in the residuals from ODS interfered with the DHA analysis. The fact that there was no difference in the DHA among concentrations implied that the concentration of contaminant was not necessarily related to the toxicity. Therefore, other factors such as chemical stabilisation or weathering of the sludge could be linked to the toxic effect as previously reported (Domene *et al.*, 2008a; Domene *et al.*, 2008b; Roig *et al.*, 2012; Alvarenga *et al.*, 2016). This finding confirmed the importance of using ecotoxicity tests combined with the chemical tests.

7.6.3. Oil and water content determination in oil sludges

The oven drying method used in this study gave information about the water and dry contents of the sludges. In addition, the organic material and solid contents were obtained from the dry content in which the organic material can be associated with the oil fraction in the sludge. It was confirmed that the ODS sample had the highest amount of solids since this was a sludge with drilling muds. Also, the method found a high organic material content for NSC, the sludge with the highest amount of oil. However, this method overestimated the amount of water found in NSC which was due to the presence of a high concentration of light hydrocarbons which were volatilised during the determination of water content at 105°C. Therefore, it is recommended to test the water content by other methods. For example, Taiwo and Otolorin (2009) and El Naggar et al. (2010) calculated the water content by co-distillation of the water with benzene following the standard procedure from the American Society for Testing and Materials (ASTM-D95-13, 2013). Also, the Karl-Fischer titration and the azeotropic distillation by the Dean-Stark method can be utilised (Jin et al., 2014; Jin et al., 2013). In this thesis, high-field NMR was used successfully as the method to confirm the oil and water content. NMR does not require any solvent, and it only needs a small quantity of sample.

High-field NMR confirmed that the water content was overestimated by the oven-drying method. The NMR data gave an overview of the oil and water contents. However, there were some issues in the NSC due to the presence of a third component detected in the CPMG T_2 decay data, besides the two components of oil and water. Further work needs to be done, and find a way on how to deal with this impurity. For instance, the fitting can be repeated for a number of times by varying the starting parameters.

7.6.4. The co-contamination in oil sludges

Since this thesis was focused on the organic chemical contamination in the sludges, there was no metal concentration data of the recovered oil and OSW residuals in our study. The trace elements were only analysed at the beginning of the study in the characterisation of oil sludges. Indeed, the complexity of this waste has been pointed out because other factors than the EPH component in the sludge were related to the toxicity. Although the PTEs were

not analysed in the OSW residuals, it could be possible that these elements were washed out by the surfactants with the residuals during the OSW. For example, this situation was with the interference of copper from the ODS residuals in the DHA test obtained in this study.

Furthermore, the role of surfactants in the removal of metals in soils has been reported before (Mulligan *et al.*, 2001; Torres *et al.*, 2012). However, there is a need to perform more studies on the treatment of heavy metals in the oil sludge as suggested by Hu et al. (2013). For instance, ion-exchange textiles can be used after the oil sludge washing to remove the heavy metals (Elektorowicz and Muslat, 2008).

7.6.5. The future direction for OSW

The main findings of this study suggested that the S/OS ratio is a crucial parameter in the OSW. Also, despite that the ORR mean values were higher for the surfactant-treated sludges, there were no significant differences whether surfactants were applied or not. Consequently, there was no a significant effect on the surfactant concentrations. Moreover, it was found that cyclohexane could be used as an alternative to more toxic solvents such as toluene, with the similar enhanced recovery efficiency and also with the added value to be a more benign to the environment co-solvent. Following this idea, RL can be used because it is more benign to the environment compared with the other surfactants. Taken together, these results can be used as the starting point for some recommendations for the OSW which are summarised in Figure 7.3.

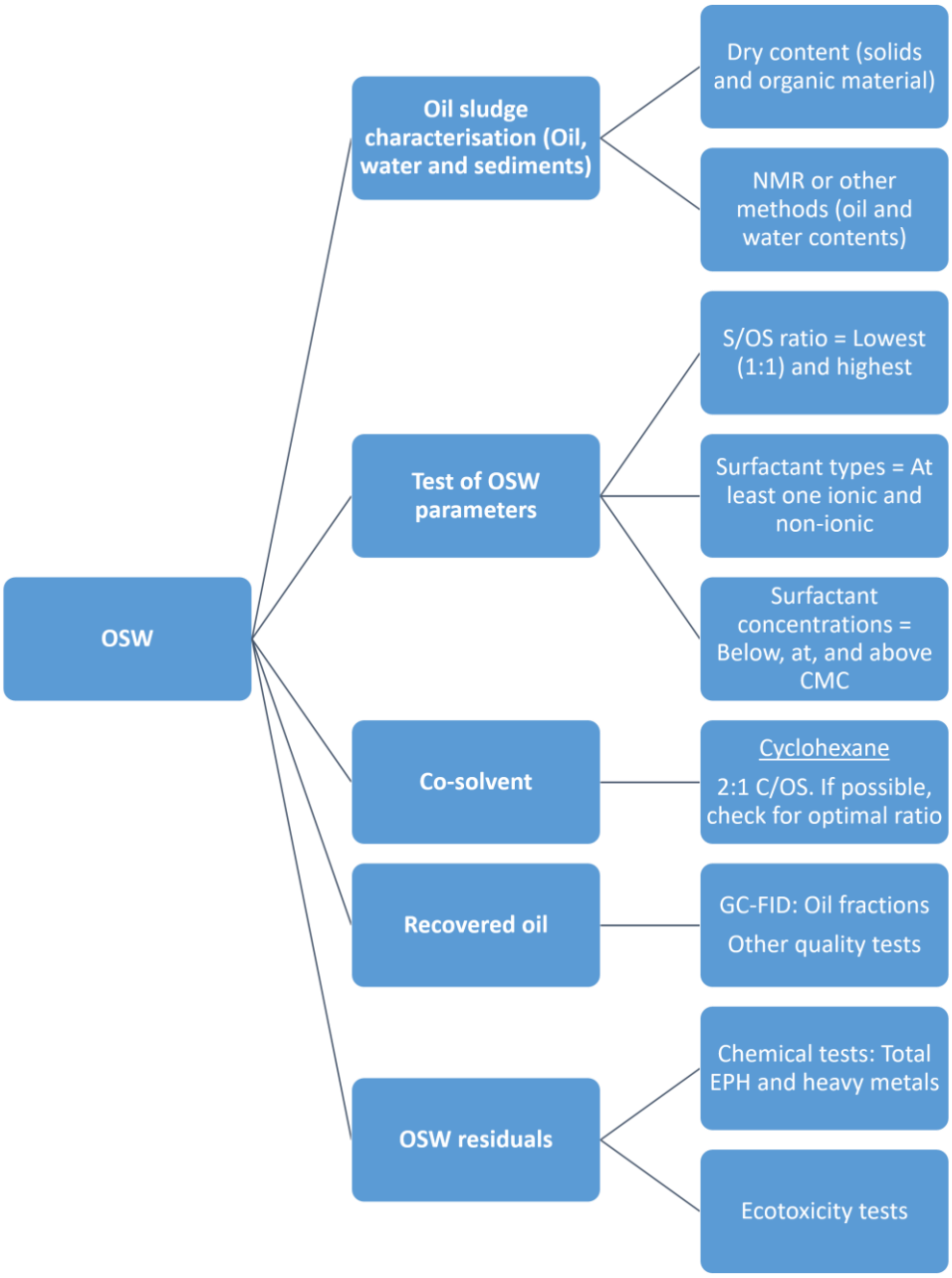

Figure 7.3. Recommendations for future applications of the OSW process as a pretreatment of oil sludges.

Before doing the OSW, the characterisation of the physicochemical properties of the sludge, including the EPH analysis of the distribution of hydrocarbon fractions, could determine if the recovered oil from OSW can be reused as a feedstock in the further refining processes (Giles, 2010). In addition, high-field NMR could be used as a non-destructive

method to assess the oil and water contents in the oil sludge. The oven-drying content can determine the dry content with the organic material and solid contents of the oil sludge.

For testing the OSW process of an oil sludge sample, firstly the OSW parameters have to be tested at a bench scale. As suggested before, the Taguchi design seems to be a reliable experimental design to be applied at this early experimental stage. It is recommended for the S/OS ratio factor to analyse only two levels at the lowest (1:1) and the highest possible ratio depending on the availability of resources. For the surfactant type, it is suggested to consider only one ionic and non-ionic surfactant, as it was demonstrated the selective recovery of oil fractions by different surfactants in this thesis. Four surfactant concentrations can be evaluated that are 0, 0.5, 1, and 5CMC. If there is not enough time or resources, it is recommended to check first with 0CMC, 0.5CMC and 5CMC, so any contaminant mobilisation or solubilisation can be detected, respectively. Also, a rapid test can detect if there are any significant differences whether surfactants are used or not. It is recommended to apply the cyclohexane at 2:1 C/OS or higher ratios if possible because the addition of more cyclohexane could improve the amount of recovered oil, as mentioned before. Hu et al. (2016) recommended adding cyclohexane at 4:1 C/OS ratio which had the highest recovery (62%) in an ultrasonic assisted solvent extraction from a tank bottom oil sludge. Since this thesis was done only at lab scale, the co-solvent was evaporated with nitrogen to know the real quantity of recovered oil. However, this is not feasible on an industrial scale. For example, the co-solvent can be distilled from the recovered oil. Then, the separated solvent vapour can be liquefied using a compressor and a cooling system, which finally is directed to a solvent recycling tank (Figure 2.5 and Section 7.7).

The recovered oil can be analysed with GC-FID to evaluate the different oil fractions. Also, quality tests can be done such as API gravity, pour and flash point, and heat of combustion (Abouelnasr and Zubaidy, 2008; Zubaidy and Abouelnasr, 2010; Hu et al., 2015). The recovered oil can be mixed with crude oil to improve its quality (Abdel Azim *et al.*, 2011). Specifically, if the recovered oil has mostly light fractions, it can be mixed with appropriate refinery by-products and used as a diesel fuel (Kuriakose and Manjooran, 1994). However, Giles (2010) recommended doing some crude oil compatibility tests such as the agglomeration of waxes or asphaltenes from both oils. This test is important because this agglomeration could lead to clogging in the oil pipelines. The two methods for assessing the compatibility of recovered oil mixtures recommended by Giles (2010) included the standard test procedures for the determination of total sediment in residual fuels (ASTM-D4870-09, 2014) and cleanliness

and compatibility of residual fuels by the spot test (ASTM-D4740-04, 2014). As an extra comment, the OSW method could be applied not just for oil recovery, but also to decrease the burden of some organic and possibly inorganic contaminants. This situation will indeed lead to a further investigation of the inorganic contamination analysis before and after OSW as mentioned before.

Finally, the test of OSW residuals is important to decide if it is necessary to treat the residuals further. Moreover, the plants used in the phytoremediation can have an economic advantage (e.g. soybeans for biodiesel production). It is important to not only rely this decision on chemical tests such as EPH and heavy metal concentrations. As some authors have mentioned previously and this thesis confirmed, the oil burden is not necessarily connected with its toxicity. Therefore, there is a need to undertake ecotoxicological tests to confirm this fact as the chemical stabilisation could make the contaminants not bioavailable. If possible, apart from the DHA and ryegrass germination toxicity tests, other methods can be applied to have a wider understanding of the toxicity in different organisms. These methods can include the earthworm mortality, inhibition of luminescence from the bacteria *Vibrio fischeri,* and the crustacean water flea *Daphnia magna* immobilisation tests (Alvarenga *et al.*, 2007; Alvarenga *et al.*, 2016).

The practical and economic feasibilities of the large-scale application of the oil sludge washing are discussed in the next section.

7.7. The practical and economic feasibilities of OSW at a large scale

This thesis has been focused on the application of oil sludge washing on a laboratory scale. According to the results of this thesis, the efficiency of this method was evidenced in the ORR values which were close to 70%. Moreover, the ORR values obtained in this thesis were much higher compared with other studies that used only solvent (30 – 40%). Due to these outstanding results in this thesis, there is a potential to apply this method at a large scale. Therefore, this section shows the practicality and costs involved in the application of this method at a large scale.

The first aspect to have in mind when applying OSW on an industrial scale is to ensure that the system is closed as mentioned by AERCO (1995). Therefore, this setup can avoid any leakage to the environment and human health (See Figure 2.5 and Section 2.7). Figure 7.4 shows the proposed diagram for the application to a large industrial scale of the oil sludge washing method used in this thesis. It has to be clarified that this is a hypothetical scenario and further studies are needed to check any technical details and issues that may rise.

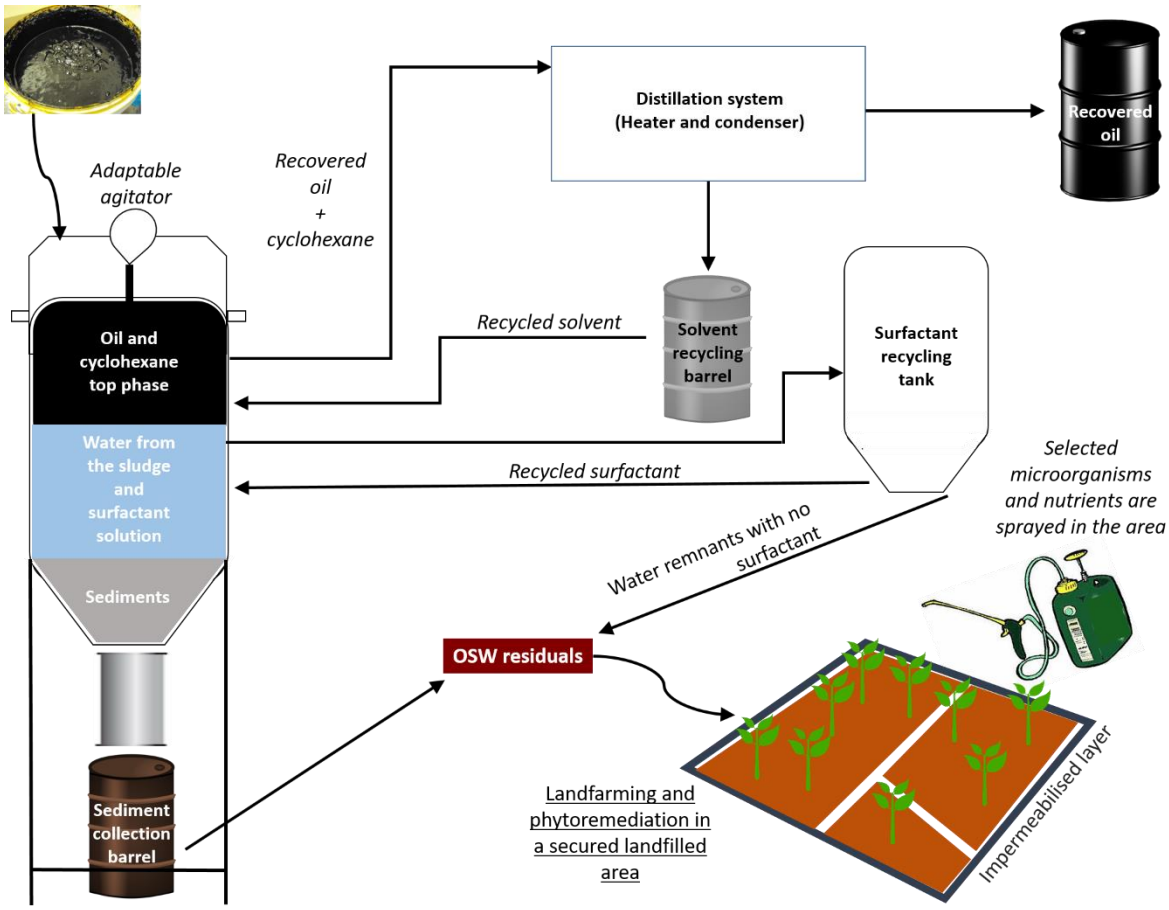

Figure 7.4. Diagram of the proposed oil sludge washing method at large scale. All pictures are free licensed by Creative Commons.

The oil sludge washing method used in this thesis consisted of four steps. First, the addition of surfactant and co-solvent (cyclohexane). Second, the mechanical shaking. Third, the gravitational separation of phases. Fourth, the separation of the cyclohexane and oil. Therefore, the proposed application of this method to a large scale starts with the OSW in a tank where the oil sludge, the surfactant, and the co-solvent are mixed. The tank has an electric mixer or

agitator to homogenise the mixture thoroughly. After the phases are separated, the top layer of the oil and co-solvent goes to a distillation system to separate the oil and the solvent. Then, the oil is recovered, and the co-solvent can be recycled and reused again for another OSW. The middle layer with the water from the sludge and surfactant solution is directed to the surfactant recycling tank so that the surfactant can be recovered and reused again in the next OSW. The residual water from the surfactant recycling step can be mixed with the sediments at the bottom layer of the OSW tank. Finally, these OSW residuals can be further treated with the landfarming and phytoremediation combined method in a designated area. If there is an option, the remaining water from the surfactant recycling can be treated in a wastewater treatment plant. More details of each step mentioning the practical and economic feasibilities are referred to in the next paragraphs.

It is important that the mixing tank (OSW tank) has a conical shape at the bottom because it can provide a better drainage of the sediments. The lid or top head of the tank has the connection to adapt the agitator and one opening to pour in the oil sludge, surfactant, and co-solvent. Moreover, it is important that the opening at the bottom is wide enough to avoid any clogging of the sediments. Also, the tank should have a flange at the bottom to connect a pipe directed to a container for sediment collection. Some companies can design the tanks under request. For instance, the cost of a stainless steel tank with a conical bottom of a capacity of 100 gal (i.e. ~ 450 L) is around 3,000 GBP (Mixer Direct). This tank has an outside diameter of 78 cm and a height of 92 cm. The cost of an electric and adaptable industrial mixer or agitator can be around £1,500 for this type of tank (Mixer Direct). The maximum mixing rotation is 1750 rpm. This rotation speed is more than enough for this case because it was reported that the mixing speed could be between 200 to 300 rpm (Peng *et al.*, 2011; Yan *et al.*, 2011). The S/OS and C/OS ratios can be calculated based on the dimensions of the tank.

The reagents used in the OSW are the surfactants (RL, TX100, and TX114) and the co-solvent (cyclohexane). The advantages of the biosurfactants are that these compounds have higher surface activity, lower toxicity, higher degradability compared to synthetic surfactants. Also, biosurfactants are stable at extreme salinities, pH, and temperatures (Torres *et al.*, 2011; Chandankere *et al.*, 2013). Even though the production of these type of surfactants is expensive, it has been reported that glucose, glycerol, olive oil, ammonium salts, urea, and *n*-alkanes can be used as an alternative substrate for the production, saving costs (Nguyen *et al.*, 2008). To date, RL is commercially available because this is used in enhanced oil recovery (EOR), bioremediation, and pharmaceutical and cosmetic formulations (Sekhon Randhawa and

Rahman, 2014). However, RL is the most expensive of the surfactants used in this thesis as the costs of production are high. For instance, only 10 mg of a high purity RL (98%) costs 175.50 GBP. Since rhamnolipids are used in the petroleum industry to cleaning tanks or for bioremediation purposes, companies are selling the product in bulk, which it cheapen the costs per kilogram. In fact, one kilogram of 90% pure rhamnolipid in solid granular state costs 500 GBP. The price for 100 kg is 36,000 GBP (360 GBP·kg^{-1}). These products are from the same company that supplied the rhamnolipid for this thesis (AGAE Technologies). In this study, the highest critical micelle concentration used for all surfactants was 5CMC. In fact, the highest ORR (76%) was obtained with RL at this concentration (Figure 7.2). Therefore, the following calculations will consider 5CMC as the surfactant concentration. The molecular weight of RL is 546 g·mol^{-1} (Table 3.1), and the CMC was 0.048 mM (Figure 3.6), the concentration of RL needed at the CMC is 0.026 g·L^{-1} and for 5CMC is 0.13 g·L^{-1}. Therefore, one kilogram can be enough to make almost 7,700 L of RL at 5CMC. Moreover, higher concentrations can be tested (e.g. 10CMC or 50CMC) to assess if there is an improvement in the oil recovery. Indeed, the ultra low CMC for RL is very advantageous because it is not necessary to add a high amount of rhamnolipid.

TX100 and TX114 are less expensive surfactants compared to RL. The cost of 1 L of TX100 and TX114 is 65 GBP and 100 GBP, respectively. This information is from the same suppliers (Sigma-Aldrich). About 1 gallon (4.5 L) of TX-100 costs 190 GBP, and 5 gallons (~23 L) are 1,000 GBP. TX114 is less expensive than TX100. In fact, 1 gallon and 5 gallons of TX114 cost 115 and 410 GBP, respectively. Also, these non-ionic surfactants had low CMC values as for TX100 is 0.28 mM (molecular weight = 625 g·mol^{-1}) and for TX114 is 0.36 mM (537 g·mol^{-1}). Therefore, these low CMCs are beneficial in terms of the preparation of the surfactant solution because it is not necessary to add a high volume of surfactant to reach the CMC. If 5CMC is used in the OSW, it is recommended to prepare an intermediate stock solution due to the viscosity of these surfactants. Therefore, 1 L of TX100 and TX114 can be diluted to make a 10% (v/v) stock solution (1 L of pure surfactant dissolved in 9 L of water to have a final volume of 10 L). For example, the volume needed for TX100 to reach 5CMC is 849 µl in a final solution of 100 ml, so only 0.08 L are needed to make a 10 L solution at 5CMC. Cyclohexane is commercially available to be purchased in high quantities. One tonne (907 kg) can cost around 1,500 GBP. This amount of cyclohexane is equivalent to having approximately 1160 L.

After the agitation, three layers are observed, a top layer with the oil and co-solvent, a middle layer with water from the sludge and surfactant solution, and a bottom layer with the sediments from the sludge. This step is critical and the most difficult to perform because the OSW tank does not have compartments inside to separate each layer. Therefore, the operator in charge should be checking visually when taking out each layer. First, the oil and co-solvent layer is taken from the tank. Since the co-solvent makes the recovered oil less viscous, this can be easily removed from the tank with an air operated pump (maximum flow rate: 80 $L \cdot min^{-1}$; suitable for use with oil) and transferred directly to the distillation system using a pipe. This type of pump costs 350 GBP (Oil and Fuel Pumps, UK). The middle layer with the water from the sludge and surfactant solution can be extracted the same way as the top layer using a pump from the top of the tank. Then, it can be transferred to the surfactant recycling tank. Finally, the sediments can be removed from the tank by opening the bottom end which is connected to the sediment collection barrel. A 210 L barrel costs 90 GBP (Oipps, UK). Before another OSW cycle starts, the recycled co-solvent and surfactant can be re-added to the OSW tank.

Regarding the solvent recycling, the option proposed by AERCO (1995) by using separately the distillation column, the compressor and the cooling can be an option. However, only an industrial distillation column can be around 10,000 GBP. Therefore, an integrated solvent recovery system seems to be a better option. Figure 7.5 shows examples of two industrial solvent recycling system that are commercially available. A general schematic diagram is shown in Figure 7.5B. The system has already incorporated a distillation bucket, the heating system to boil the solvent and a cooling apparatus to condense the solvent again into a liquid state. The liquid can be recovered into a barrel, and the oil can be recovered from the distillation bucket or boiler. This system is much easier to operate as it is all contained in one machine. The system proposed by AERCO (1995) can be more expensive as all the components have to be bought separately (e.g. distillation column, compressor, cooler). Moreover, the costs can increase with the assembly of all of these components. Figure 7.5A and B show one type of solvent recovery system with a working capacity of 250 L and a total boiler capacity of 410 L. This system is from a UK supplier (Solutex Ltd.). It works with a water cooler condenser. Also, it has an internal scraper system for cleaning the boiler. This is important as the oil can be recovered in this system. The distillation temperature ranges between 50 – 200°C (for reference, cyclohexane has a boiling point of 81°C). The distillate output (i.e. volume of recycled solvent) is 40 to 65 $L \cdot h^{-1}$ which varies depending on the solvent and recovered oil percentage. In the case of cyclohexane, its boiling point is low, so it is

expected a higher distillate output rate. According to the supplier (Solutex, UK), this system costs 55,000 GBP. Figure 7.5C shows another solvent recovery system from a supplier in China (Hongyi Environmental Equipment Co.). In general, the structure is the same as the system sold by the UK supplier, but it works with an air-cooling system for condensation instead of water. It has a working capacity of 250 L. The distillate output is 70 $L \cdot h^{-1}$. This system has a feeding device which has a pneumatic feeding pump for an automatic addition of the recovered oil and solvent into the system. This machine costs 15,000 GBP. Even though it is less expensive than the other system, this cost does not include shipment fees and the vacuum device (~2,000 GBP), which can increase the costs. However, since cyclohexane is intended to be used it is not necessary to have a vacuum device as the boiling point of this solvent is less than 150°C. A 210 L barrel similar to the sediment collection barrel can be used to collect the recycled solvent. This barrel costs 90 GBP (Oipps, UK).

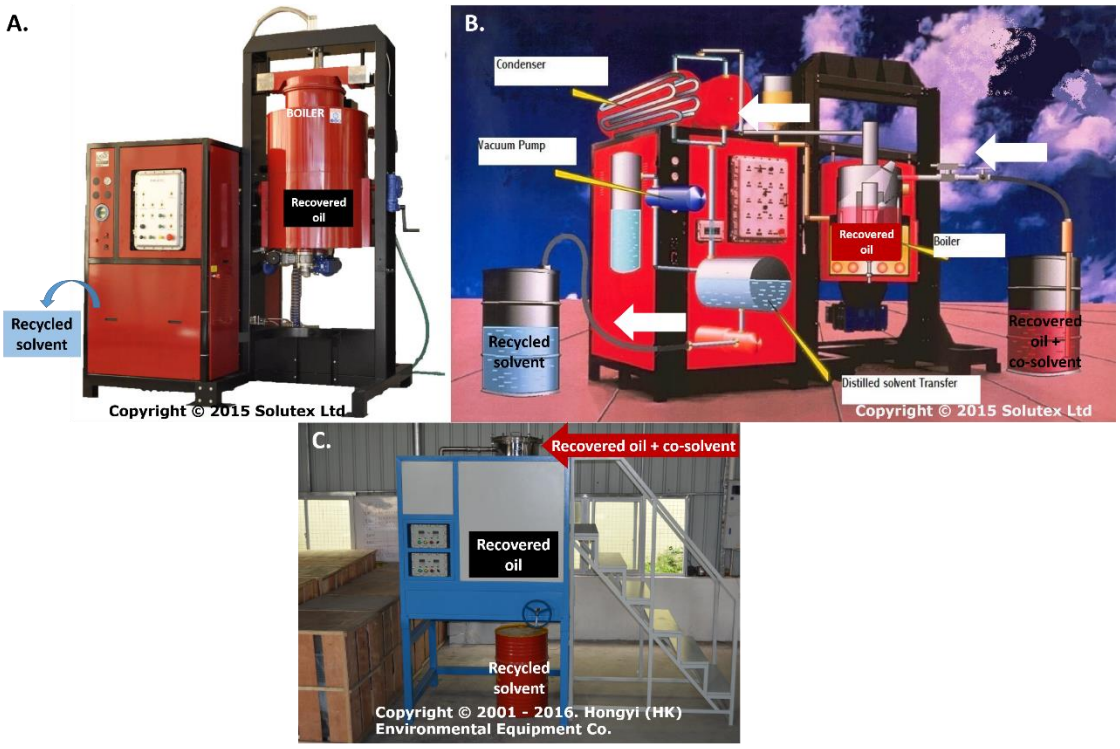

Figure 7.5. Pictures of solvent recycling systems from two companies. A) Distillation system with a working capacity of 250 L. B) Diagram of the internal mechanism with the water cooler condenser. C) Distillation system from another supplier with a working capacity of 250 L and an air-cooling condenser system.

Biosurfactants had high ORR values in this thesis, so these compounds can be used as these are more benign to the environment compared to synthetic surfactants. Also, TX114 and TX100 showed high oil recovery rates. Therefore, the three surfactants have the potential to be used in the ORR. After the OSW, the recycling of these surfactants can be advantageous for saving costs. In fact, it is possible to recycle them as it was proposed for the solvents. In the case of TX114 and TX100, the recovery can be done by heating the surfactant to reach its cloud point where a surfactant-rich phase is obtained. The cloud point for TX100 is 64 – 65°C and for TX114 is 20 – 25°C (Arnold and Linke, 2007). If it is not possible to reach these temperatures, especially for TX100, the cloud point can be reduced by adding salts. To decrease the cloud point of TX100 to room temperature, it can be added 9 – 23% $(NH_4)_2SO_4$ (ammonium sulphate) or 16 – 25% NaCl. On the contrary, the cloud point of TX114 can be decreased to 4°C with 20% of glycerol if needed (Fricke, 1993). The separation can be achieved by waiting for several hours depending on the surfactant solution, or this separation can be accelerated by centrifugation if necessary (Arnold and Linke, 2007). However, it is recommended to wait until the separation is achieved, so the costs do not increase with the centrifuge. The surfactant-enriched phase can be on either the top or the bottom of the tank depending on its density.

For the case of biosurfactants, included rhamnolipids, the cloud point approach cannot be done as these surfactants are stable even at extreme temperatures as mentioned before. Once a suitable production method is found, biosurfactants can be applied at large scale so that the costs can be reduced. Biosurfactants can be recovered by acid precipitation and micellar-enhanced ultrafiltration (MEUF) (Wang and Mulligan, 2009). The acid precipitation consists in the centrifugation of the solution with the biosurfactant and the adjustment of the pH to 2 by adding concentrated HCl. Then, it is necessary to add dichloromethane (Mulligan *et al.*, 1999; Sakthipriya *et al.*, 2016). The MEUF method consists on the filtration of the micelles of rhamnolipids using ultrafiltration cells (Mulligan and Gibbs, 1990). However, its application is only on a laboratory scale. Since the acid precipitation requires the addition of HCl and dichloromethane, this will increase the costs, and also the generation of more waste. Therefore, it is recommended only to apply the surfactant recycling for the TX100 and TX114 as it is much easier and more feasible to do. Even though it is very complex to recover the rhamnolipid, it can be worth it to assess if the recycling of the biosurfactant is more cost-effective compared with the production or purchase of more rhamnolipid. As mentioned before, the production of biosurfactant is expensive. A stainless steel tank smaller than the OSW tank can be used. A 30 gallon (130 L) tank can be used is 1,800 GBP (Mixer Direct). This tank can have a top lid and

an opening at the conical bottom similar to the OSW tank for an easy collection of the surfactant-enriched and residual water phases. The tank has an outside diameter of 50 cm and a height of 60 cm. The remnant water with no surfactant can be mixed with the sediment from the OSW tank, so these can be considered as the OSW residuals.

The OSW residuals can be treated by landfarming and phytoremediation in a designated area isolated with an impermeable layer to avoid leachates to the groundwater (Figure 7.4). The microorganisms for bioremediation are commercially available in the United Kingdom. However, 20 L of a bioremediation formula costs £400 (EnviroCleano Ltd.). Bento et al. (2003) mentioned the importance of using indigenous microorganisms from the sludge because it is expected that these microorganisms can survive and degrade the contaminants in the sludge. These microorganisms can be selected by the replica method (Villegas-Torres *et al.*, 2011). This method consists of selectively pressuring the isolated microorganisms from the residual water and sludge in some consecutive sub-cultures in mineral salt medium with the sludge as the sole carbon source. Then, the selected consortia of microorganisms can be added by spraying the liquefied agar medium with the desired inoculum size of microorganisms. The inoculum size can be 10^8 CFU (colony-forming units) per gram of soil (Trindade *et al.*, 2005). Therefore, there is enough inoculum of microorganisms to achieve the bioremediation purposes. The bioaugmentation (i.e. addition of nutrients for the microorganisms) can be applied based on the C:N:P ratio (carbon:nitrogen:phosphorus) of 100:10:1 which was reported as optimal for microbial activity (Morgan and Watkinson, 1992; Zucchi *et al.*, 2003; Beolchini *et al.*, 2010). Ammonium sulphate [$(NH_4)_2SO_4$] and monopotassium phosphate (KH_2PO_4) can be added as the nitrogen and phosphorus sources, respectively (Rojas-Avelizapa *et al.*, 2007; Fonti *et al.*, 2015). It is required to do a physicochemical analysis of the OSW residuals-amended soil to know the concentrations of each element before adjusting this ratio. The cost of 25 kg of ammonium sulphate for industrial and fertiliser purposes is 40 GBP (Mistral Industrial Chemicals). For the monopotassium phosphate, the cost of 25 kg is 50 GBP (JFC Monro). A polyethylene geomembrane can be used as the impermeable layer in the designated area. The square meter of this type of geomembrane with a gauge thickness of 0.50 mm or 0.75 mm is 4 GBP·m^2 or 5 GBP·m^2 (Geosyn thetic Technology Ltd., UK). For example, if the designated site has a maximum length, width, and depth of 25 m, 25 m, and 0.60 m, respectively, the approximated volume to fit 375 m^3. The total cost of the 0.5 mm polyethylene geomembrane needed for this area is 3,000 GBP. The area of the land is 625 m^2.

The selected plant species can be germinated first in a greenhouse and then transplanted to the designated area. As proposed in this thesis, soybeans can be used as the phytoremediator species because this species can used for soybean production. Then, a profit can be obtained. The soybean seeds (30) cost 4 GBP (Jungle Seeds, UK).

Table 7.1 shows an example of the costs of materials and the apparatus for the application of the proposed OSW method at an industrial scale. In this case, the capacity of the OSW tank is 450 L. The costs were based on the values mentioned earlier in this section.

Table 7.1. Costs of apparatus and materials for the oil sludge washing for a large scale considering an OSW tank with a capacity of 450 L.

		Item	Cost (GBP)
Oil sludge washing at large scale (450 L)	Apparatus	OSW tank: Stainless steel tank (450 L)	3,000
		Adaptable agitator	1,500
		Air operated pump	350
		Distillation system	15,000
		Sediment collection barrel (210 L)	90
		Solvent recycling barrel (210 L)	90
		Surfactant recycling tank (130 L)	1,800
		TOTAL	21,830
	Reagents	90% pure rhamnolipid solid granular (1 kg)	500
		TX100 (1 ga = 4.5 L)	190
		TX114 (1 ga = 4.5 L)	115
		Cyclohexane (1 ton = 907 kg)	1,500
		TOTAL	2,305
Landfarming and phytoremediation of OSW residuals (Total land area = 625 m^2)	Materials	Bioremediation formula (20 L)	400
		0.5 mm geomembrane for a 625 m^2 area	3,000
		Ammonium sulphate (75 kg)	120
		Monopotassium phosphate (75 kg)	150
		Soybean (30 seeds)	4
		TOTAL	3,674

***** These costs include the recycling of solvent and surfactant. Also, the general costs of treatment of OSW residuals by bioremediation and phytoremediation are shown.

These calculations are only to have an idea of how much will cost to perform the process. Indeed, more costs can raise depending on the final technical issues (e.g. piping needed to connect the tanks and ensure a closed system). The total cost of the oil sludge washing using an OSW tank with a capacity of 450 L is approximately 24,000 GBP, including the expenses for solvent and surfactant recycling. However, the value decreases drastically to 7,000 GBP if only the cost of the OSW with TX114 and cyclohexane is considered without the expenses for surfactant and solvent recycling. Moreover, this value can decrease further as not all the one tonne of cyclohexane and surfactant solution is used in one OSW cycle. Considering that the OSW tank has a total volume capacity of 450 L (0.45 m^3), the maximum amount of oil sludge that can be treated is about 0.15 m^3. Then, the ratio of co-solvent : surfactant : oil sludge can be kept at 1:1:1. Since this maximum amount of oil sludge that can be treated is in volume units, it cannot be compared with the values of the other treatments mentioned in the literature review (Section 2.6). However, this hypothetical example can be used as an idea of the costs for adequating the OSW at an industrial scale. Also, a final cost of the treatment of oil sludge per tonne of oil sludge can be given only after performing several cycles of OSW to establish the efficiency of the method. Moreover, this final cost will depend on the sludge, as some sludge will need a different S/OS ratio to maximise the oil recovery.

In case that it is necessary to treat the OSW residuals, the general costs for a bioremediation and phytoremediation schemes in in the example from Table 7.1 (375 m^3) are approximately 4,000 GBP. According to JRW Bioremediation (2017), the total cost of a bioremediation project in the United States can vary between 10 GBP to 30 GBP·m^3. For the hypothetical example mentioned in this section, the minimum cost of treatment can be 3,750 GBP which are 10 GBP·m^3. However, this value can increase with some phytoremediation-related costs such as the materials needed to keep the plants, and the costs involved to adequate the area. Regarding the production of biodiesel, approximately 3.5 kg of soybean oil is required to produce one gallon of biodiesel (Carriquiry and Babcock, 2008). According to Klein et al. (2016), the budget for soybean production in Nebraska, USA, can be approximately 45 GBP per m^2 including field operations, services, and materials, and land insurance.

There are some ways for saving more costs. As mentioned earlier (Section 2.7), the adaptation of the treatment process in the same area where the oil sludge is stored can save time and costs on transportation. Also, TX114 is much less expensive compared to RL and TX100, and this synthetic surfactant has the potential to be easily recovered by reaching the cloud point.

In conclusion, the surfactant and co-solvent recovery steps have to be carefully considered because the apparatus needed is considerably expensive. For instance, only 30% of the costs is for performing only the OSW, and the remaining 70% is for costs of the surfactant and co-solvent recycling systems. However, if the proposed OSW method is used intensively, it can be true that the investment can be recovered after several OSW cycles, the profit obtained with the recovered oil as feedstock for fuel production, and the potential production of biodiesel.

7.8. Final comments

This thesis confirmed that OSW is a promising and rapid pretreatment technique which can recover the oil and also reduce the load of organic contaminants in the residual sludge. Moreover, it was studied in detail the interaction of the surfactant type, surfactant concentration and S/OS ratio in the oil recovery from oil sludges obtained from different sources. As an added value, it was demonstrated that the S/OS ratio factor was crucial in the OSW which makes a significant difference in the oil recovery depending on the oil sludge. Surprisingly, it was found that the surfactant concentration did not have an effect on the oil recovery, and moreover, the addition of surfactant was not significantly different in most of the oil sludges analysed. RL, TX100, and TX114 were the surfactants with high oil recovery rates. In general, the ORR values ranged from 50 to 70% using these surfactants. These ORR values were higher compared to other studies (30 – 40%). As reported before, RL can be used as the selected surfactant due to its lower toxicity and CMC value, and higher surface activity. Cyclohexane, a more benign co-solvent, was confirmed to have a comparable ORR values to toluene, a commonly used co-solvent. Also, it was demonstrated that the contaminant burden is not always proportional to the toxicity, as the OSW residuals can be chemically stable reducing the bioavailability of the contaminants. As an added methodological procedure, high-field NMR could be a rapid and promising technique to check the oil and water contents in the oil sludges. Also, it was demonstrated that alternative experimental designs could quickly test and detect the interactions effects of the OSW factors while reducing the number of experimental runs. Indeed, this facilitated the experimental work in this thesis due to the high amount of parameters to test. Finally, the practical and economic feasibilities of the application of the OSW method were evaluated in a hypothetical large-scale scenario. A detailed explanation was

given mentioning the material and apparatus needed. If a surfactant and solvent recycling systems are used, the costs can increase dramatically due to the expensive machinery. In fact, only 30% of the costs is for the OSW process, and 70% is for surfactant and co-solvent recycling systems expenses. Therefore, it is recommended to carefully analyse the costs before applying these systems to the OSW. A profit can be obtained by reusing the recovered oil as a feedstock for fuel production. Moreover, if the OSW residuals are treated by landfarming and phytoremediation, soybeans can be profitably used for biodiesel production.

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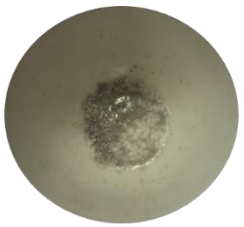
Appendix A: Physicochemical characteristics of oil sludges (cont.)

Table A 1. Oil sludge samples before, after heating at 105°C for 24 h (water content) and 550°C for 30 min for solid content determination.

	Original sludge	Water content (105°C for 24 h)	Solid content (550°C for 30 min)
WSS			
ODS			
STS			
RS			
NSC			

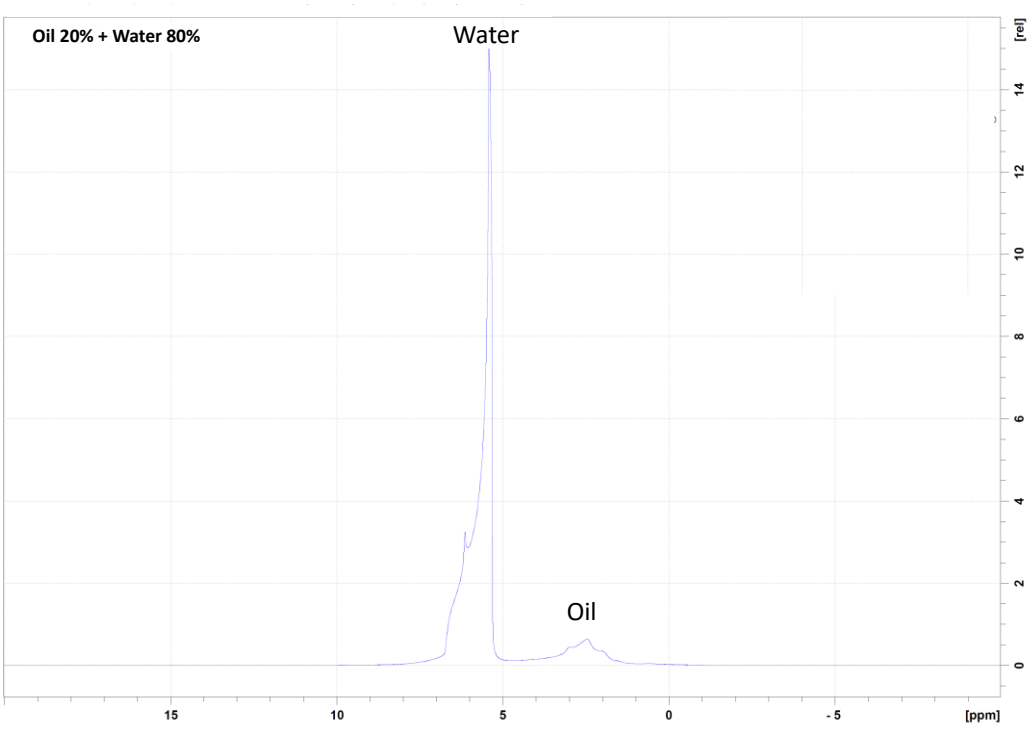


Figure A. 1. 1H spectra for the oil (20%) and water (80%) mixture standard.

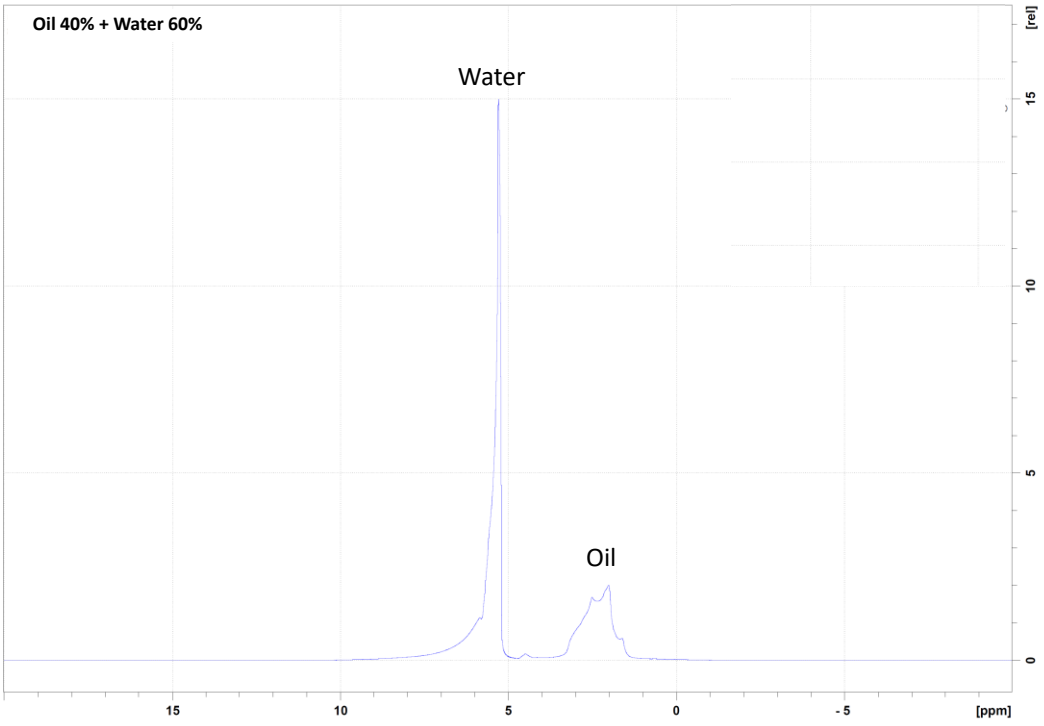


Figure A. 2. 1H spectra for the oil (40%) and water (60%) mixture standard.

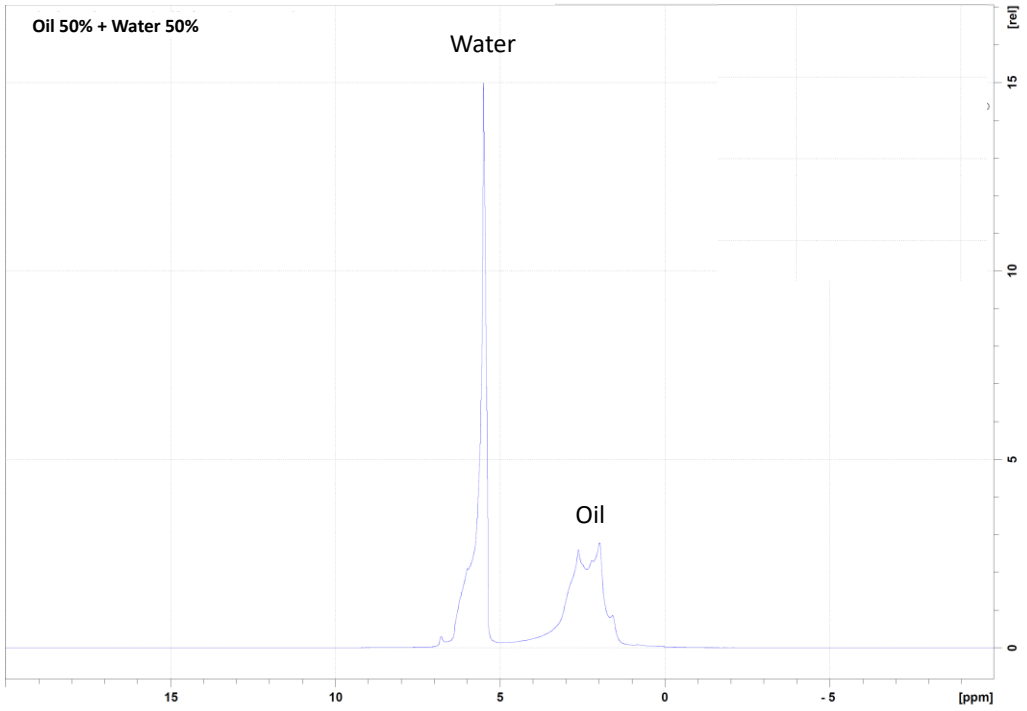


Figure A. 3. 1H spectra for the oil (50%) and water (50%) mixture standard.

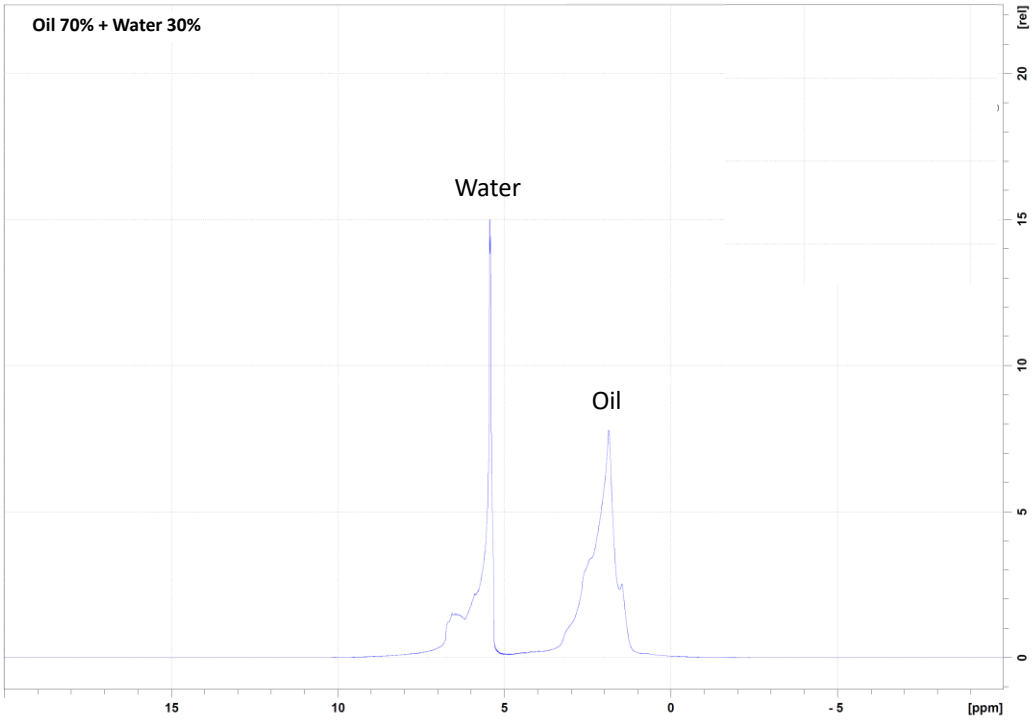


Figure A. 4. 1H spectra for the oil (70%) and water (30%) mixture standard.

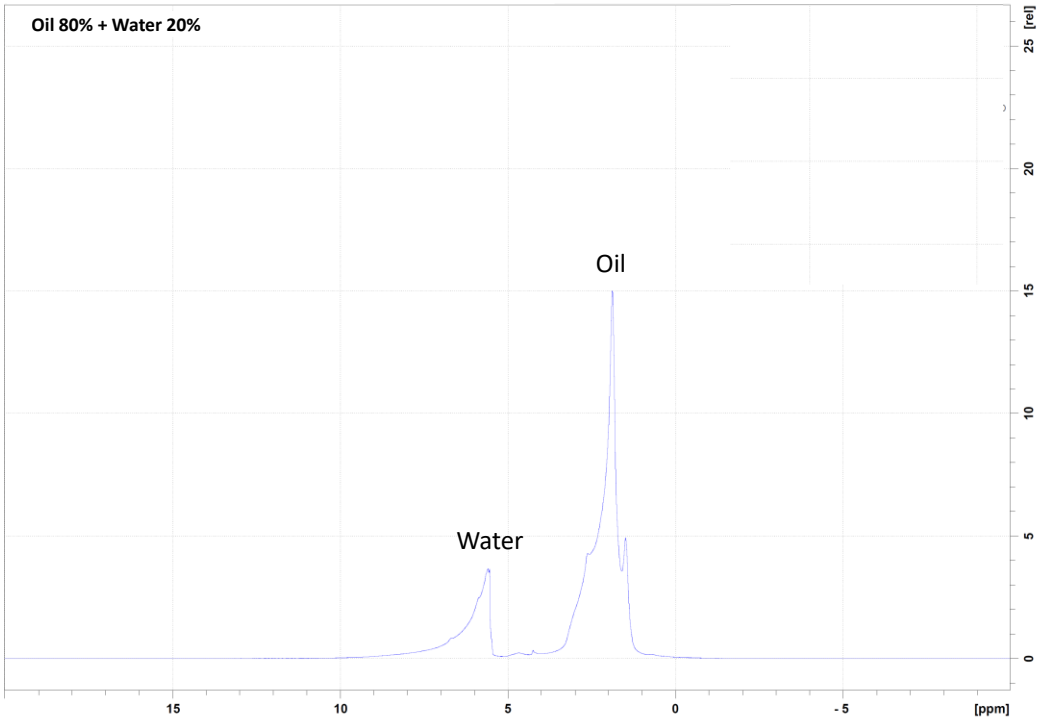


Figure A. 5. 1H spectra for the oil (80%) and water (20%) mixture standard.